CRYSTAL FIELD ASPECTS OF THE VIBRATIONAL SPECTRA OF SOME METAL COMPLEXES OF TROPOLONE AND NITROGEN DONOR LIGANDS

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by

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C O N T E N T S.

SUMMARY

Previous work on crystal field aspects of the vibrational spectra of metal β-ketoenolates has been extended here to metal tropolonate complexes. The crystal field trends have been used to assist in the assignment of metal sensitive vibrations to the transition metal tropolonate complexes.

A study has been made of the effects of spin state and Jahn-Teller distortion on the vibrational spectra of the metal tropolonates. Of particular interest is the octahedral divalent metal tropolonate adducts, where the distortion of the copper complex is small, and the metal 2-thiotroponates where the Jahn-Teller distortion is absent.

The spectra of the lanthanide tropolonates are of interest, as a plot of the metal sensitive vibrations show the 'double-humped' curve indicating that crystal field effects are present in the lanthanide ions. This has not previously been shown. Further, from the vibrational spectra of the various lanthanide tropolonates, various conclusions are made regarding structure.

The non-transition metal tropolonates provide a system devoid of crystal field effects and afford the opportunity to investigate the influence of other factors on the vibrational spectra. Of interest is the strong influence of the ionic radius and ionization potential on the metal sensitive vibrations, and the remarkably small influence of the mass of the metal ion on these vibrations.

Although the vibrational spectra of complexes of ethylenediamine and N- substituted ethylenediamines were studied, difficulty with assignment of the metal sensitive vibrations and the complicating influence of substituents on the spectra, prevents any observations made, from being conclusive.

Parts of this work have been published as follows:

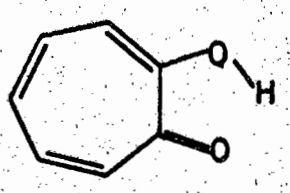
1. J.M. Haigh, R.D. Hancock, L.G. Hulett and D.A. Thornton, J. Mol. Structure, *4* (1969) 369. "Crystal Field Aspects of Vibrational Spectra.II. First-row Transition Metal(II) Complexes with Nitrogen Donors".

2. L.G. Hulett and D.A. Thornton, Spectrochim. Acta, *27A* (1971) 2089. "Infrared Spectra of First Transition Series Metal Tropolonates."

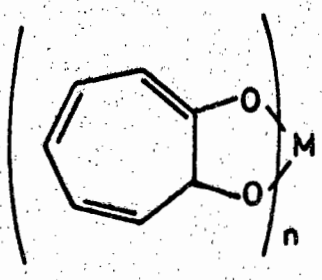
3. L.G. Hulett and D.A. Thornton, Chimia, *26*(1972) 72. "Infrared Spectra of Tetrakis(tropolonato) Lanthanide(III) Chelates: Evidence for Crystal Field Effects".

4. L.G. Hulett and D.A. Thornton, J. Mol. Structure, in press. "Crystal Field Aspects of Vibrational Spectra. V. Evidence for Crystal Field Effects from the Infrared Spectra of Lanthanide(III) Tropolonates".

Structures of Complexes Appearing in Text.

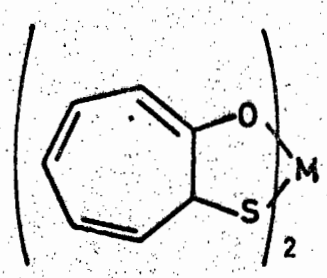


Tropolone (HT).

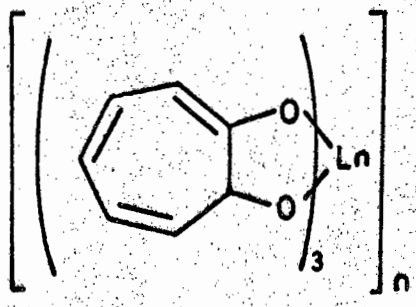


n=2; Divalent metal tropolonates (MT_2).

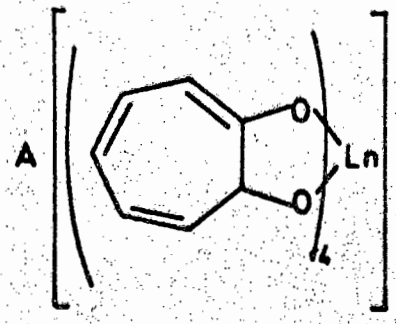
n=3; Trivalent metal tropolonates (MT_3).



Divalent metal thiotroponates ($M(ST)_2$).

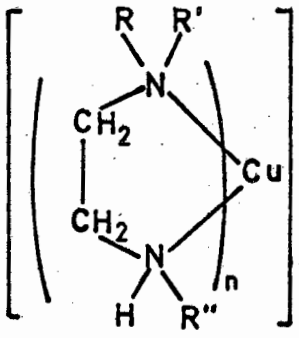


Tris lanthanide tropolonates (LnT_3).



(A=Li, Na)

Tetrakis lanthanide tropolonate salts ($[LnT_4]^-$).



X_2 (X = Cl, Br)

n = 1; Mono ethylenediamine copper complexes.

n = 2; Bis ethylenediamine copper complexes.

R = R' = R'' = H; ethylenediamine (en).

R = CH_3; R' = R'' = H; N-methylethylenediamine (NMeen).

R = CH_2CH_3; R' = R'' = H; N-ethylethylenediamine (NEten).

R = $CH_2CH_2CH_3$; R' = R'' = H; N-propylethylenediamine (NPren).

R = R' = CH_3; R'' = H; N,N-dimethylethylenediamine (asym) (NNMeen).

R = R'' = CH_3; R' = H; N,N'-dimethylethylenediamine (sym) (NN'Meen).

I. INTRODUCTION.

1. CRYSTAL FIELD ASPECTS OF VIBRATIONAL SPECTRA.

Crystal field theory (CFT) is based on the splitting of the inner orbitals of a metal ion by the field of the ligands surrounding it. This field may be considered to arise from electrostatic repulsion between the electrons of the ligand orbitals and the metal orbitals in the line of closest approach with the ligands (CFT), or as a result of chemical bonding between the metal cation and the ligands (ligand field theory and molecular orbital theory). The electrostatic repulsion gives rise to orbitals of differing energies. This results in metal complexes having varying stabilities according to the electron population of the split orbitals.

Theoretically, it should be possible to have the CF splitting of orbitals in any element which contains partially filled *p*, *d* or *f* orbitals. The *p* shells are precluded however as the bonding of the *p* orbitals of an element involves considerable interaction with the orbitals of the other atom in the bond and the *p* orbitals lose their identity. The *d*, and particularly the *f*, orbitals of an element in a chemical compound bear a close resemblance to the orbitals in the free ion, to enable CFT to be applicable. In *d* orbitals the splitting is large and the associated stabilization may be as much as 100 k cal/mole, while for *f* orbitals the splitting is much smaller and the associated stability is of the order of ten or twenty times smaller than for *d* orbitals. It is therefore natural that the most studied systems are those consisting of compounds containing elements with partially filled *d* orbitals. The *d* orbitals will therefore be treated

in more detail to provide some insight into CFT.

The amount by which the orbitals are split determines the associated stabilization energy of the metal complex. Ligands with strong fields cause greater splitting of the *d* orbitals and thus give rise to a greater stabilization energy. This energy is referred to as the crystal field stabilization energy (CFSE). In the splitting of the *d* orbitals of a metal ion in an octahedral environment, three orbitals (t_{2g}) are stabilized and two orbitals (e_g) are destabilized. For the total energy to remain constant, each t_{2g} orbital is stabilized by $^2/5$ of the total splitting energy (10 Dq) and each e_g orbital is destabilized by $^3/5$ of 10 Dq. The amount of CFSE that occurs for any octahedral metal ion with partially filled *d* orbitals is given by the expression,

$$CFSE = -(0.4n_t - 0.6n_e)\,10\ Dq \qquad (1)$$

where n_t and n_e are the number of t_{2g} and e_g electrons in the metal ion and 10 Dq is the energy difference between the t_{2g} and e_g orbitals. 10 Dq can be expressed as

$$10\ Dq = \delta g \qquad (2)$$

whence

$$CFSE = -(0.4n_t - 0.6n_e)\,\delta g \qquad (3)$$

where g is the spectroscopically determined magnitude of 10 Dq for the octahedrally hydrated metal ion, while δ measures the CF splitting power of the ligand relative to the splitting power of water taken as unity[1].

The CFSE is actually only a small contribution to the total bonding energy of a metal complex. The total energy will incorporate such effects as the attraction of the metal ion for the ligands and the interelectronic repulsions (other than *d* orbital electrons). Although CFSE is small compared to some of these other effects, these other effects

vary linearly through a series of complexes in which the transition metal ion is varied from d^0 to d^{10}, so that the CFSE is superimposed on a reasonably constant, or uniformly varying energy system. It is thus possible to distinguish CF effects from others which occur simultaneously.

CFT has been successful in explaining many of the properties of transition metal compounds[1,2]. This is particularly true of their electronic spectra, magnetochemistry and chemical thermodynamic properties (such as lattice energies, heats of hydration and heats of formation). An estimation of the contribution of CF effects to the stability of a series of transition metal complexes is approached in thermodynamic studies by plotting a thermodynamic parameter against the atomic number of the metal ion, across the series. Effects other than the CF effect, such as ionic contraction, are considered to vary approximately linearly with increase in atomic number and therefore do not influence (qualitatively) any deviations caused by the CFSE.

The heterolytic bonding energy ($-\Delta H$) of complex formation[2], in the gas phase, from the free ions corresponds to the equation

$$M^{n+}_{(g)} + nL^{-}_{(g)} \rightarrow ML_{n(s)} \qquad -\Delta H \qquad (4)$$

for an ion M of valency n with a bidentate monobasic ligand L. The heterolytic bonding energy may be divided into a CFSE contribution ($-\delta H$) and an ionic contraction contribution (E_r) and may be expressed as

$$-\Delta H = -\delta H - E_r \qquad (5)$$

In order to obtain a value for the CF contribution ($-\delta H$) from the measured energy ($-\Delta H$) for any particular complex, it is necessary to know the value of $-E_r$ for that complex. There

are certain metal ions where the CFSE is zero (namely metal ions with d^0,d^5 and d^{10} electron configurations, where the amount of stabilization is countered by an equal amount of destabilization) and in these instances

$$-\Delta H = -E_r. \qquad (6)$$

If $-E_r$ increases linearly, then in a plot of $-\Delta H$ against atomic number, interpolation between these points (d^0,d^5 and d^{10}) enables values of $-E_r$ to be estimated for all metal ion configurations. Thus using these estimates for $-E_r$ values of the CFSE ($-\delta H$) can be obtained. (Example of this, pertaining to lattice energies and heats of hydration can be found in the review by George and McClure[2]).

Little has been done, until recently, to correlate the changes observed in vibrational spectra of a series of transition metal complexes, where the metal ion is varied, with the trends predicted by the CFSE. The frequencies of the vibrational spectra are dependent on some mode of vibration of the molecule. These vibrations are determined by the strengths of the vibrating bonds and thus any change in bond strength will influence the force constant and hence the frequency of the related vibrations (assuming negligible mass effect). The metal-ligand bond strengths are dependent upon the CFSE of the particular complex, variations in CFSE being associated with corresponding variations bond strength. Thus the metal sensitive frequencies of a series of metal complexes - that is those which incorporate some vibration involving metal-ligand bonds - should show some correlation with the CFSE. As the CFSE influences the metal-ligand bond strength, it seems probable that the metal sensitive frequencies of a series of complexes would exhibit a variation with d orbital population

similar to that shown by thermodynamic properties.

This has been shown for a series of di-and trivalent transition metal complexes[3-5]. It has been shown that for a number of series of different β-ketoenolate systems there exist some frequencies (which can be assigned to metal-ligand vibrations) which parallel the predicted trend indicated by CFT. Almost without exception, the predictions of the CFT are mirrored by the observed trends of the metal sensitive vibrations. Further, metal-ligand vibrations assigned in the literature are seen to parallel CFSE trends[6] for various series of nitrogen donor complexes and the argument can be extended to account not only for CFSE trends, but also deviations from these expected trends caused by structural changes occurring where various metal ions assume differing geometries.

It has therefore been established that metal sensitive vibrations, for a series of transition metal complexes, all follow the predicted CF trend. It should be possible to use this trend to assign metal sensitive frequencies to new series of compounds, where metal sensitive frequencies have not previously been assigned.

The purpose of this work is to assign the metal sensitive frequencies in the vibrational spectra of a series of transition metal tropolonate complexes and then to use these assignments to investigate the vibrational spectra of other systems involving tropolone as a ligand. Further, knowing where the metal sensitive frequencies occur, it might be possible, by studying non-transition metal tropolonates, to deduce factors other than CFSE which influence the metal sensitive frequencies. Finally by comparing the vibrational

spectra of a series of divalent metal complexes of ethylenediamine and N- and N,N'-substituted ethylenediamines it might be possible to deduce some information on the effects of substituents on the metal sensitive vibrations.

2. METAL TROPOLONATES

Tropolone (2,4,6-cycloheptratriene-1-one-7-ol) is an α-ketoalcohol which binds metal ions through the two oxygen atoms. The unsaturated seven-membered carbon ring confers a certain rigidity to the molecule that renders it inflexible, so that the bite between the two oxygen atoms is relatively fixed. As the bite is between two α-oxygen atoms it will be comparatively narrow (relative to the more flexible β-ketoenolate ligands).

The small bite of the tropolone ligand presents the possibility of synthesizing metal complexes of high coordination number. This fact has led to a comprehensive study of metal tropolonates[7-12] in an attempt to prepare complexes with high coordination number. A wide range of complexes have been synthesized including some transition metal complexes, non-transition metal complexes and complexes with the lanthanide metals. Many of these complexes have been studied in terms of their intractability to various solvents and predictions pertaining to their structure have been made, particularly in cases where intermolecular interactions occur to produce oligomeric complexes. Certain inferences have been made on the basis of vibrational spectra, but these involve the carbonyl and carbon-carbon stretching frequencies. Deductions made on the basis of these frequencies

must be viewed with some scepticism as many of these assignments are, in the light of subsequent work, doubtful. These publications provide an excellent guide to the field of metal tropolonates particularly as regards their synthesis and structure.

Some work has been done on the formation constants of metal tropolonates[13-15]. As is the case with studies of this kind on other systems, many different metals have been used and the determinations by each group of workers have been performed under different conditions. Little has been said about any trends observed for the formation constants of the tropolonates. The most recent publication on formation constants[15] examines the interrelationship between log k_1 and e^2/r which produces a linear plot for all the non-polarizable metals. It can be seen from the results obtained, that the values for the divalent transition metal complexes follow the Irving-Williams stability order[16].

Not much work has been done on the vibrational spectra of the metal tropolonates. Ikegami[17-19] has produced a series of publications dealing with the vibrational spectra of tropolone and other related compounds. On the basis of shifts in the spectra on deuteration and shifts caused by changing the phase of the tropolone or the solvent (for solutions), assignments are made of some bands to various modes of vibration. The assignments tend to agree with those made by Koch[20] who based his assignments on comparisons with allied systems and other related compounds.

The only work on the vibrational spectra of metal tropolonates is the study[21] of the effect of [^{18}O]-labelling of bis(tropolonato) copper(II) (CuT_2). This study has enabled

several assignments to be made with some certainty. These include the assignment of the two bands in the 1500-1600 cm^{-1} region to $\nu C=C$ and not carbonyl frequencies. A band in the 1300-1360 cm^{-1} region is assigned to $\nu C-O$ which corresponds to the long bond length of the C-O bond found in tropolone complexes[22-24]. The labelling study also enables several metal sensitive bands to be identified below 700 cm^{-1}.

Thus there is sufficient knowledge of the vibrational spectrum of CuT_2 to enable a comparison to be made with the assignment of metal sensitive bands on the basis of CFT.

3. DIVALENT METAL ETHYLENEDIAMINE COMPLEXES

A vast amount of work has been done on complexes of ethylenediamine and substituted ethylenediamines with various divalent metal salts. Included in this work have been several publications dealing with the vibrational spectra of these complexes[25-35].

These publications tend to concentrate on two aspects of the vibrational spectra. One aspect is the difference in band patterns observed for complexes of different metal salts[25-28]. This difference was first thought to be caused by a change in the configuration of the bound ethylenediamine ligand, but crystallographic studies have shown[26] that this difference does not exist.

The other aspect of the vibrational spectra which has received attention is that of the assignment of metal-ligand vibrations. The spectra below 700 cm^{-1} have several bands which shift both on change of metal ion and on deuteration of the $-NH_2$ groups. Since not all the spectra

are determined for the whole range (some publications only record spectra as low as 400 cm^{-1} [25-28] a full assessment of this region is not possible in every case. The earlier work tended to favour the assignment of the band in the 500-550 cm^{-1} region as νM-N[25-33]. However this band and others in this region are also present in the vibrational spectra of the ligands. Also as these bands shift on deuteration of $-NH_2$, which does not directly influence the M-N bond, it seems likely that these vibrations are the result of coupling between ligand vibrational modes and metal-ligand vibrations. This could account for the sensitivity to change in metal ion and deuteration of $-NH_2$. It has been proposed[34-35] that the metal-ligand vibration does not occur in the 500-550 cm^{-1} region, but in the 300-400 cm^{-1} region. There are no ligand vibrations in this region so that the possibility of this vibration being coupled with a ligand vibration is less than for the other bands. However, all these bands show metal sensitive characteristics to some degree and it is impossible to assign any one particular band to νM-N. The band in the 300-400 cm^{-1} region does have an advantage in that it does not change its pattern when N- substituents are introduced to the ligand. In the other regions this often causes a change in the pattern of the bands rendering it impossible to study any substituent trends.

The purpose of this study of the vibrational spectra of the divalent metal ethylenediamine complexes is to further investigate the problem of the assignment of metal sensitive bands. These bands can be assigned by studying a series of complexes where the CF effect is operative. Further, it

might be possible to assign the metal sensitive bands for compounds containing N- substituted ethylenediamines and, by assigning these bands, to observe what effect these substituents have on the metal-ligand bonding.

II. EXPERIMENTAL.

1. PHYSICAL METHODS.

(i) Vibrational Spectra.

Vibrational spectra were determined on a Beckman IR-12 spectrophotometer which had been calibrated against CO_2 and H_2O. Samples were in the form of nujol mulls pressed between either CsBr or CsI plates. Where nujol frequencies obscured those of the compounds, hexabutadiene was used as a mulling agent. Various sampling techniques had previously been tested, including CsI and KBr pellets and solution spectra in $CHCl_3$. The mull spectra were found to be the most satisfactory. The spectrophotometer has a resolution better than 0.5 cm^{-1} in the 1000-200 cm^{-1} region, better than 1.0 cm^{-1} in the 2000-1000 cm^{-1} region and better than 2 cm^{-1} in the 4000-2000 cm^{-1} region. All frequencies were obtained from the wavenumber drum of the spectrophotometer, and not read from the chart paper, for maximum precision. In cases where the shift in frequencies were very small (the lanthanide tropolonates), these frequencies were determined five times and reproducibility was always found to be better than 0.5 cm^{-1}.

(ii) Ultraviolet-Visible Spectra.

The UV spectra were recorded on a Beckman DK-2A ratio recording spectrophotometer. The compounds were examined as $CHCl_3$ solutions using the transmission mode and as solids, supported on filter discs in the reflectance mode. The spectra obtained from both these methods were similar.

(iii) Magnetic Moment Determinations.

These were performed at 293°K on a Stanton-Newport Gouy balance. The procedure used was that described by Figgis and Lewis[36] for the determination of the magnetic moments of solids. The instrument was calibrated using $Hg[Co(CNS)_4]$.

2. PREPARATION OF COMPOUNDS.

(i) The Non-Transition Metal Tropolonates.

The alkali metal tropolonates were prepared by mixing molar proportions of tropolone dissolved in methanol and the alkali hydroxide dissolved in as little water as possible. The solution was heated and the precipitate filtered and dried in vacuo at 80°C. The compounds could not be analysed due to the difficulty involved in analysing compounds containing alkali metal ions.

The alkaline earth tropolonates were prepared by the literature method[11]. The alkaline earth metal chloride and tropolone were dissolved in methanol-water solution and triethylamine added to produce a yellow precipitate which was filtered and dried in vacuo at 100°C for 12 hours. The group III and IV metal complexes were prepared by the literature method[7] which involved adding tropolone dissolved in methanol to the metal salt in water and filtering the precipitate.

(ii) The Transition Metal Tropolonates.

The tropolonates of the transition metal ions were prepared by literature methods[7,9,11,37,38] except for VT_3, CrT_3, CoT_3 and RuT_3 which were prepared by methods similar to those used for the analogous acetylacetonate (AA) metal complexes[39-42]. TiT_3 and VT_3 were sensitive to oxygen and

were handled throughout in a nitrogen atmosphere. The dihydrate of NiT_2 was removed by filtering before sublimation in the preparation of the anhydrous NiT_2. The pyridine adducts of NiT_2 and ZnT_2 were prepared by dissolving the anhydrous complex in pyridine and then precipitating the adduct by addition of diethyl ether. The 2,2'-bipyridine(bipy) and 1,10-phenanthroline(phen) adducts were prepared by dissolving the MT_2 complexes in chloroform with the addition of bipy or phen and then precipitating with petroleum ether. An excess of bipy or phen was added in the case of CuT_2. This method is similar to that used for the analogous AA adducts[43].

2-Thiotropone was prepared from 2-chlorotropone[44]. The complexes were prepared by adding a solution of the metal acetate in water, to the thiotropone dissolved in methanol. The Ni, Cu and Zn complexes have been previously described[11,44,45].

(iii) The Lanthanide Tropolonates.

Both the tris tropolonates and the tetrakis tropolonates of the lanthanide ions have been previously reported[9]. The starting material for the LnT_3 complexes in all cases was Ln_2O_3 which was dissolved in HCl to form the chloride, washed with water to remove the acid and then redissolved in water and added to tropolone dissolved in methanol. Of all the tetrakis salts, only $Na[LaT_4]$ did not form, which concurs with the findings of previous workers[9] who were also unsuccessful in their attempts to synthesize this compound.

(iv) Ethylenediamine Complexes.

The ethylenediamine and N- substituted ethylenediamines divalent metal complexes are prepared by adding the ligand to a methanolic solution of the metal salt. The precipitate that forms is filtered and dried in vacuo. When the precipitate does not form immediately it is necessary to reduce the volume of methanol by heating the solution for a short period. Both the Cu and Ni complexes have previously been prepared[34,46-49].

3. RESULTS.

(i) Microanalytical Data.

TABLE 1. Analysis results of the non-transition metal tropolonates.

Compound	Colour	Calculated %C	Calculated %H	Found %C	Found %H
Mg T_2	Yellow	63.1	3.8	63.7	5.9
Ca T_2	Yellow	59.6	3.6	59.5	3.6
Sr T_2	Yellow	50.9	3.0	50.4	3.2
Ba T_2	Yellow	44.3	2.6	42.9	2.7
Al T_3	Brown	64.7	3.9	64.9	3.8
Ga T_3	Buff	59.3	3.4	58.5	3.5
In T_3	Buff	52.8	3.2	52.8	2.8
Sc T_3	Buff	61.7	3.7	62.3	3.8
Y T_3	Buff	55.7	3.3	55.1	3.4
La T_3	Buff	50.3	3.0	50.7	2.7
Cd T_2	Yellow	47.1	2.8	47.5	2.8
Hg T_2	Yellow	38.0	2.3	37.7	2.1
Tl T	Yellow	25.8	1.5	25.5	1.4
Pb T_2	Yellow	37.4	2.2	37.2	2.3
Pb T_4	Orange/ Brown	48.6	2.9	47.7	2.8
Bi T_3	Yellow	44.1	2.6	44.0	3.1
Bi T_2 Cl	Cream	34.5	2.1	34.1	2.0

TABLE 2. Analysis results of the transition metal tropolonates.

Compound	Colour	Calculated			Found		
		%C	%H	%N	%C	%H	%N
Mn T_2	Yellow	56.6	3.4	-	56.1	3.5	-
Co T_2	Orange	55.7	3.3	-	56.0	3.4	-
Ni T_2	Green	55.8	3.3		55.6	3.4	-
Cu T_2	Olive	55.0	3.3	-	54.9	3.4	-
Zn T_2	Buff	54.7	3.3	-	54.8	3.4	-
Ti T_3	Green	61.3	3.7	-	60.5	4.6	-
V T_3	Green	60.9	3.7	-	61.6	4.0	-
Cr T_3	Purple	60.7	3.6	-	60.9	3.5	-
Mn T_3	Dark Green	60.2	3.7	-	60.8	3.6	-
Fe T_3	Red	60.2	3.6	-	60.1	3.6	-
Co T_3	Green	59.8	3.6	-	59.8	3.9	-
Ni T_2.2py	Green	62.8	4.4	6.1	62.3	4.8	6.2
Zn T_2.py	Yellow	59.0	3.9	3.6	58.4	3.8	4.0
Mn T_2.bipy	Orange	63.9	4.0	6.2	63.4	4.3	5.9
Co T_2.bipy	Red	63.3	4.0	6.2	63.8	5.4	6.4
Ni T_2.bipy	Green	63.3	4.0	6.2	62.2	3.9	6.4
Cu T_2.bipy	Green	62.7	3.9	6.1	61.9	3.8	6.2
Zn T_2.bipy	White	62.4	3.9	6.1	62.0	3.7	6.1
Mn T_2.phen	Orange	65.4	3.8	5.9	65.1	3.6	5.9
Co T_2.phen	Red	64.9	3.7	5.8	64.5	3.7	5.9
Ni T_2.phen	Green	64.9	3.7	5.8	63.9	3.8	6.0
Cu T_2.phen	Green	64.3	3.7	5.8	63.7	3.5	6.0
Zn T_2.phen	White	64.0	3.7	5.7	63.5	4.0	5.8
Ru T_3	Red	54.3	3.3	-	53.4	3.3	-
Rh T_3	Orange	54.1	3.2	-	53.9	3.2	-
Co(ST)$_2$	Black	50.4	3.0	-	50.9	3.4	-
Ni(ST)$_2$	Purple	50.5	3.0	-	50.0	3.0	-
Cu(ST)$_2$	Brown	49.7	3.0	-	48.3	3.0	-
Zn(ST)$_2$	Yellow	49.5	3.0	-	49.5	3.3	-
NiHFA$_2$.bipy	Green	40.5	1.5	4.3	39.1	1.7	4.9
CuHFA$_2$.bipy	Green	40.2	1.5	4.3	39.3	1.7	4.5

TABLE 3. Analysis results for the tris(tropolonate) lanthanides.

Complex	Colour	Calculated %C	Calculated %H	Found %C	Found %H
La T_3	Buff	50.3	3.0	50.7	2.7
Ce T_3	Yellow	50.1	3.0	49.7	3.1
Pr T_3	Pale Yellow	50.0	3.0	50.4	3.1
Nd T_3	White	49.7	3.0	50.3	3.3
Sm T_3	Buff	49.2	3.0	49.3	3.1
Eu T_3	Pale Yellow	48.9	2.9	48.6	3.0
Gd T_3	Pale Yellow	48.5	2.9	49.1	2.9
Tb T_3	Buff	48.3	2.9	48.2	3.0
Dy T_3	Buff	48.1	2.9	47.7	2.9
Ho T_3	Yellow	47.8	2.9	48.3	3.0
Er T_3	Yellow	47.5	2.9	48.1	2.9
Tm T_3	Buff	47.3	2.8	46.9	2.9
Yb T_3	Yellow	47.1	2.8	47.6	2.8
Lu T_3	Yellow	46.9	2.8	46.5	3.2

TABLE 4. Analysis results for metal complexes of ethylenediamine and substituted ethylenediamines.

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Mn(en)_3]SO_4$[a]	21.8	7.3	25.4	21.0	7.0	25.8
$[Co(en)_3]SO_4.H_2O$	20.4	6.8	23.8	19.9	7.0	22.4
$[Ni(en)_3]SO_4$	21.5	7.2	25.1	21.6	7.3	24.8
$[Cu(en)_3]SO_4$	21.2	7.1	24.7	21.5	7.2	24.3
$[Zn(en)_3]SO_4$	21.1	7.0	24.6	20.8	7.1	24.7
$[Cu(en)_2]Cl_2$	18.9	6.3	22.0	18.3	6.6	22.5
$[Cu(en)_2]Br_2$	14.0	4.7	16.3	14.4	4.9	15.9
$[Cu(en)Cl_2]$	12.3	4.1	14.4	12.5	4.0	14.3
$[Cu(en)Br_2]$	8.5	2.8	9.9	8.7	3.2	10.9
$[Cu(DAP)_2]Cl_2.H_2O$[b]	23.9	7.3	18.6	24.5	7.1	18.1
$[Cu(DAP)_2]Br_2$	19.4	5.4	15.1	21.3	6.2	14.3
$[Cu(DAP)Cl_2]$	17.3	4.8	13.4	17.0	5.0	12.9
$[Cu(DAP)Br_2]$	12.1	3.4	9.4	12.0	3.1	9.3
$[Cu(NNMeen)_2]Cl_2$[c]	30.9	7.8	18.0	30.2	7.7	17.6
$[Cu(NNMeen)_2]Br_2$	24.0	6.1	14.0	23.8	6.0	13.4
$[Cu(NNMeen)Cl_2]$	21.6	5.4	12.6	20.8	5.3	12.8
$[Cu(NNMeen)Br_2]$	15.4	3.9	9.0	15.7	3.8	8.8
$[Cu(NN'Meen)_2]Cl_2.H_2O$[d]	29.2	7.9	17.0	29.0	8.0	16.5
$[Cu(NN'Meen)_2]Br_2$	24.0	6.0	14.0	24.2	6.1	14.0
$[Cu(NN'Meen)Cl_2]$	21.6	5.4	12.6	21.1	5.2	12.6
$[Cu(NN'Meen)Br_2]$	15.4	3.9	9.0	15.3	3.9	9.2
$[Cu(NMeen)_2]Cl_2$[e]	25.5	7.1	19.8	25.5	7.2	19.8
$[Cu(NMeen)_2]Br_2$	19.4	5.4	15.1	19.4	5.3	15.2
$[Cu(NMeen)Cl_2]$	17.3	4.8	13.4	17.4	4.9	13.3
$[Cu(NMeen)Br_2]$	12.1	3.4	9.4	12.1	3.4	9.5
$[Cu(NEten)_2]Cl_2$[f]	30.9	7.8	18.0	30.6	7.7	18.0
$[Cu(NEten)_2]Br_2$	24.0	6.0	14.0	24.0	6.0	13.6
$[Cu(NEten)Br_2]$	15.4	3.9	9.0	15.5	3.9	8.7
$[Cu(NPren)_2]Cl_2$[g]	35.5	8.3	16.5	35.4	8.4	16.6
$[Cu(NPren)_2]Br_2$	29.5	6.9	13.8	28.3	6.6	13.3
$[Ni(en)_2]Cl_2$	19.3	6.5	22.4	19.5	6.8	23.0
$[Ni(en)_2]Br_2$	14.2	4.8	16.5	14.1	4.7	16.6
$[Ni(DAP)_2]Br_2$	19.1	5.3	14.9	19.1	5.9	14.4
$[Ni(NNMeen)_2]Cl_2.H_2O$	29.7	8.0	17.3	30.2	8.2	17.6
$[Ni(NN'Meen)_2]Br_2$	24.3	6.1	14.2	24.4	6.2	14.2

TABLE 4 continued ...

a. en = ethylenediamine; b. DAP = 1,3- diaminopropane;

c. NNMeen = N,N- dimethylethylenediamine (assym);

d. NN´Meen = N,N´- dimethylethylenediamine (sym);

e. NMeen = N- methylethylenediamine;

f. NEten = N- ethylethylenediamine;

g. NPren = N- propylethylenediamine.

(ii) Vibrational Spectral Data.

TABLE 5. Vibrational spectral data for the alkali and alkaline earth metal tropolonates. Nujol. 2000-200 cm^{-1}.

LiT	NaT	KT	RbT	TlT	MgT_2	CaT_2	SrT_2	BaT_2
1652								
1602	1611	1605	1601	1597	1595	1597	1668	1603
1522	1535	1533	1534	1518	1517	1520	1540	1532
1430	1433	1454	1446	1416	1449	1435	1450	1452
1419	1418	1429	1435	1395	1437	1417	1418	1417
1373	1381	1382	1388	1365	1368	1345	1369	1370
1252	1244	1235	1231	1234	1247	1245	1236	1239
						1239		
1228	1221	1223	1220	1222	1227	1228	1223	1218
1078		1062	1060		1078	1074	1080	1075
				996	995	999	991	
982	982	976	973	972	975	974	975	976
912	908				917	913	901	901
881	883	876	870	873	875	879	877	877
746	730	738	733	732	767	768	767	736
726	722	716	724		736	734	729	722
662	685	676	672	681	697	695	692	692
604	601	603	605	604	602	601	606	601
573	545	542	536	574	583	561	553	547
470	469	460	455	472	529	487	475	468
418	412	413	415	414	410	406	396	384
395	373	367	368	372	359	378	378	378

TABLE 6. Vibrational spectral data for group IIIB, IVB and VB metal tropolonate complexes. Nujol. 2000-200 cm^{-1}.

AlT_3	GaT_3	InT_3	SnT_4	PbT_4	PbT_2	BiT_3	BiT_2Cl
1597	1593	1597	1597	1593	1596	1595	1598
1532	1521	1521	1523	1508	1514	1517	1520
1436	1438	1428	1430	1428		1431	1432
1424	1417	1417			1411	1410	1412
1365	1359	1358	1347	1364	1346	1356	1331
1259	1266	1271	1275	1262	1261		1257
1230	1259	1240	1234		1240	1244	1224
1221	1227	1215	1221	1229	1224	1227	1210
1081	1081	1082	1078	1080	1075	1075	1077
1023	1018	1022					
1007	1007						
967	972	980	974	976	974	975	978
	945	955	951				
928	926			927	937	933	932
878	878	878	881	878	877	877	878
867	836						
770	761	755	755	740	739	763	776
732	728	731				736	726
724	713	706	722	703	697	697	710
620	607	607	625	597	585	570	536
					515	527	527
590	582	557	586	537	498	495	513
477	425	420	426	497	411	411	416
420	407	411	339	417			
384	310						

TABLE 7. Vibrational spectral data for first transition series divalent metal tropolonates. Nujol. 2000-200 cm^{-1}.

CaT_2	MnT_2	CoT_2	NiT_2	CuT_2	ZnT_2
1597	1601	1601	1600	1595	1598
1520	1522	1523	1519	1522	1517
1435	1441	1444	1436	1435	1445
1417	1419	1418	1417	1417	1415
1345	1341	1340	1340	1347	1341
1245	1251	1256	1251	1250	1253
1239			1235	1234	
1228	1226	1226	1223	1224	1224
1074	1077	1077	1078	1078	1077
999	1007	1008	1010	1001	1006
	990			990	990
974	976	976	973	973	975
913	921	918	916	922	918
879	877	878	879	877	877
			858	853	
768	765	763	761	755	763
734	735	733	731	735	734
695	699	698	703	714	698
561	587	592	611	639	590
487	517	530	545	589	533
406	416	417	425	424	416
379	382	382	391	405	382
				334	

TABLE 8. Vibrational spectral data for the first transition series trivalent metal tropolonates. Nujol. 2000-200 cm^{-1}.

ScT_3	TiT_3	VT_3	CrT_3	MnT_3	FeT_3	CoT_3	GaT_3
1596	1592	1591	1591	1593	1593	1589	1593
1527	1524	1520	1518	1517	1522	1519	1521
1437	1430	1423	1423	1430	1431	1428	1438
1418	1415	1412	1415	1416	1416	1412	1417
1361	1354	1345	1354	1333	1359	1350	1359
1346	1334	1320		1317	1346	1310	1306
1265	1265	1252	1261	1265	1265	1272	1266
1232	1225	1242	1256	1245	1232	1260	1259
1212	1213	1211	1223	1210	1219	1218	1227
1080	1081	1077	1077	1079	1078	1080	1081
1022	1022	1022	1012	1020	1021	1012	1018
		1010	1008			1005	1007
975	973	969	972	976	970	972	972
955	958				957	940	945
932	925	926	923	928	925	920	926
877	877	877	877	875	877	879	878
835	827	862	835	835	835	840	836
756	757	767	767	753	755	760	761
726	731	740	739	730	737	737	735
712	719	732	721	708	711	727	713
583	596	621	627	611	594	656	607
				592			
				583			
544	541	557	565	528	555	585	582
420	430	419	429	427	417	452	425
344	348	375	405	410	405	406	407
		317	361	338	325	373	310

TABLE 9. Vibrational spectral data for the second transition series trivalent metal tropolonates. Nujol. 2000-200 cm^{-1}.

YT_3	RuT_3	RhT_3	InT_3
1600	1593	1591	1597
1528	1520	1520	1521
1443	1430	1429	1428
1407			1417
1336	1347	1340	1358
	1269	1262	1271
1249	1235		1240
1220	1220	1213	1215
1074	1080	1080	1082
1004	1023	1006	1022
974	973	975	980
935			955
923	927	925	
877	880	879	878
767		760	755
735	740	737	731
	728	727	718
704			706
571	658	663	607
495	568	580	557
413	428	430	420
	406		411

TABLE 10. Vibrational spectral data for the lanthanide tris(tropolonate) complexes. Nujol. 2000-200 cm^{-1}.

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1597	1599	1597	1598	1598	1599	1598	1599	1599	1598	1597	1599	1598	1596
1523	1522	1524	1527	1528	1528	1528	1528	1524	1528	1523	1519	1522	1524
1437	1444	1439	1437	1438	1438	1440	1440	1443	1433	1442	1467	1460	1460
												1435	1438
1406	1410	1407	1407	1406	1406	1405	1407	1408	1409	1414	1414	1419	1412
1338	1340	1338	1338	1338	1339	1338	1339	1336	1333	1329	1330	1332	1332
1246	1247	1247	1247	1247	1249	1248	1248	1248	1250	1256	1256	1358	1257
1222	1224	1222	1221	1221	1221	1221	1220	1220	1221	1224	1223	1231	1225
1073	1073	1073	1072	1072	1074	1073	1074	1074	1076	1076	1074	1076	1078
974	975	975	974	974	974	975	974	974	975	975	973	974	973
930	931	930	932	933	933	933	934	933	935				
921	922	922	922	922	922	922	923	923	923	925	923	923	925
876	877	876	876	877	877	877	877	877	877	877	877	878	877
766	767	765	767	767	767	768	768	768	768				
730	732	731	730	730	731	730	730	730	736	735	734	736	738
698.5	699	699.5	700	701	701.5	701	702	703	703	704	706	706	706
558.5	560	561	562.5	565	567	565.5	567	569.5	570.5	572	572.5	574.5	571
511.5	513	515.5	5.7	520	523	521.5	525	526	527.5				
479.5	480.5	482.5	484	487	490	487.5	491	492.5	494.5	504	506.5	509.5	509
406	407	407	407.5	409	410	409	410.5	411	412	412.5	413	414.5	413
388	388.5	389	388.5	389	389.5	388	392	391	390	393	389	390	391

TABLE 11. Vibrational spectral data of the lithium salts of the lanthanide tetrakis(tropolonate) ions.

Nujol. 2000-200 cm^{-1}.

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1598	1599	1597	1597	1599	1599	1599	1599	1599	1600	1600	1600	1600	1600
1519	1517	1522	1515	1521	1518	1518	1518	1522	1519	1523	1524	1523	1521
1437	1435	1440	1432	1437	1440	1437	1436	1438	1438	1435	1439	1442	1444
1357	1360	1362	1359	1363	1365	1366	1368	1368	1368	1370	1371	1371	1371
1249	1249	1249	1250	1251	1251	1251	1251	1251	1252	1253	1355	1253	1254
1229	1230	1230	1230	1231	1231	1231	1231	1231	1231	1232	1232	1232	1232
1075	1075	1076	1075	1076	1078	1076	1078	1076	1077	1077	1077	1077	1077
1002	1000	1002	1001	1002	1001	1001	1002	1001	1002	1003	1003	1003	1002
977	977	978	977	977	978	978	978	978	978	977	978	977	977
920	920	921	920	920	920	920	920	920	920	920	920	919	920
876	876	876	876	877	876	876	876	876	876	876	876	876	876
764	764	765	765	765	765	766	765	766	766	767	766	766	767
737	735	737	733	738	737	736	737	738	738	738	738	738	737
698	699	700	699	700	701	701	701	702	702	702	703	703	704
581	581	582	583	584	583	583	584	582	586	583	586	581	582
490.5	492	494.5	496	499	502	500	504	505.5	506.5	508.5	510.5	512.5	512.5
440	439	439	439	439	437	438	434	431	429	431			
422	422	423	422	422	422	422	424	422	423	424	427	427	424
381	383	383	384	385	387	386	387	387.5	388	389	389	389	389
363	368	362	362.5	362	362	364	363	361	361	362	361	361	361
339	338	338	337	338	339	335	338	338	339	338	338	338	338

TABLE 12. Vibrational spectral data for the sodium salts of the lanthanide tetrakis(tropolonate) ions.

Nujol. 2000-200 cm^{-1}.

Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1596	1596	1595	1596	1595	1596	1596	1598	1599	1595	1596	1597	1595
1519	1517	1518	1518	1517	1517	1518	1519	1519	1521	1518	1521	1519
1411	1410	1407	1406	1410	1409	1409	1410	1410	1413	1411	1414	1425
1368	1371	1368	1345	1365	1365	1370	1369	1372	1368	1370	1373	1369
1241	1239	1239	1239	1240	1240	1240	1242	1242	1242	1242	1243	1243
1221	1221	1220	1221	1225	1221	1221	1221	1222	1226	1226	1226	1226
1075	1074	1075	1075	1075	1075	1076	1075	1076	1077	1076	1077	1076
1002	1002	1000	1002	1003	1001	1002	1002	1002	1000	1002	1002	1000
974	975	975	975	975	975	975	975	975	974	974	974	974
917	915	917	919	917	918	917	918	918	919	917	918	922
876	875	874	875	874	875	875	874	875	875	875	875	875
731	735	733	734	735	736	737	738	739	738	740	740	738
697	697	696	698	697	697	698	698	699	700	699	700	700
597	597	597	596	597	597	597	597	598	596	597	597	597
559	564	563	564	565	565	567	567	571	570.5	568	569	571
486	488	489.5	493	495.5	493.5	498	499.5	501	503	504.5	506	506.5
393	394	396	401	398	399	400	403	412	409	401	402	402
								401	401			

TABLE 13. Vibrational spectral data for the divalent metal tropolonate 2,2'-bipyridine adducts. Nujol. 2000-200 cm^{-1}.

Mn	Co	Ni	Cu	Zn
1594	1592	1595	1595	1594
1520	1522	1522	1524	1523
1432	1430	1438	1440	1430
1372	1370	1370	1370	1370
1318	1317	1315	1316	1317
1241	1243	1243	1244	1241
1228	1223	1227	1230	1227
1175	1175	1175	1177	1178
1156	1162	1161	1158	1160
1058	1065	1055	1058	1059
1016	1021	1025	1022	1021
973	973	972	972	973
921	919	918	920	920
875	875	876	876	876
760	761	762	761	762
745	742			744
737	736	736	737	737
733	730	732		
690	692	695	696	691
652	653	653	653	655
604	590	601	606	605
585	577	578	590	582
			552	
509	517	523	505	520
411	418	418	440	415
			419	
401	409	411	413	411
264	262	289	289	238
235		263		

TABLE 14. Vibrational spectral data for the divalent metal tropolonate 1,10-phenanthroline adducts.

Mn	Co	Ni	Cu	Zn
1592	1592	1594	1594	1595
1520	1519	1520	1522	1522
1428	1429	1430	1437	1431
1367	1367	1369	1371	1372
1350	1349	1346	1346	1347
1320	1323	1320	1318	1320
1242	1244	1243	1244	1244
1230	1230	1232	1231	1233
1146	1146	1146	1145	1147
1104	1106	1107	1104	1105
973	973	972	973	973
	955			
920	921	918	921	922
874	875	877	876	876
849	847	847	845	847
769	770	772	770	773
748		743	742	744
		734	734	734
730	730	728	729	728
693	693	695	700	692
639	642	644	639	641
	598	602	606	594
			552	
508	518	528	506	522
441	445	449	444	442
423	426	426	421	423
402	403	410	411	409
			398	
380	381	380	378	380
269	262	293	291	243
		260	250	

TABLE 15. Vibrational spectral data for the adducts of nickel and zinc tropolonate and the metal (hexafluoroacetylacetone) 2,2'-bipyridine adducts. Nujol. 2000-200 cm^{-1}.

$NiT_2 \cdot 2H_2O$	$NiT_2 \cdot 2py$	$ZnT_2 \cdot py$	$Ni(HFA)_2 \cdot bipy$	$Cu(HFA)_2 \cdot bipy$
1599	1594	1598	1655	1667
1518	1515	1518	1604	1606
	1446		1563	1559
1412	1428	1415	1534	1534
	1367	1368	1495	1499
1342	1353		1355	1348
1256	1245	1250	1318	1316
1231	1230	1233	1260	1267
1214	1224	1221	1201	1210
1077	1070	1072	1150	1155
	1040	1046	1101	1092
1018	1012	1015	1047	1047
997	998		1032	1037
976	976	975	980	983
	954	960	952	948
912	904	913	795	795
877	877	876	767	773
856	855		744	742
747	766	761	737	734
	738	752	672	678
724	725	740	640	645
704	703	704	589	588
	632	638		580
608	599	597	530	528
546	528	543	487	473
	436	426	416	416
414	407	408	394	388
395	389	380	290	295
			261	

TABLE 16. Vibrational spectral data for the metal (thiotroponate) complexes. Nujol. 2000-200 cm^{-1}.

Co	Ni	Cu	Zn
1590	1592	1596	1596
1492	1497	1495	1492
1420	1427	1420	1425
1414	1412	1413	1414
1370	1371	1376	1375
1260	1267	1252	1270
1238	1232	1241	1243
1227	1224	1233	1231
1085	1086	1082	1086
1008	1011	998	1007
943	943	931	943
923	926		905
882	884	888	879
860	852	865	855
770	756	766	760
755	734	725	723
722			
699	694	697	694
693	683		
623	650	614	
611	613	596	597
566	575	560	554
443	460	441	444

TABLE 17. Vibrational spectral data for divalent metal tris(ethylenediamine) sulphate complexes. Nujol. 2000-200 cm^{-1}.

Mn	Co	Ni	Cu	Zn
1600	1594	1597	1599	1601
1456	1457	1456	1456	1456
1341	1340	1339	1337	1341
1278	1277	1277	1278	1277
1042	1041	1041	1044	1044
976	977	980	954	978
870	874	876	879	874
			852	
672	692	709	735	693
			696	
613	615	615	613	614
515	527	534	537	524
490	501	508	517	499
			487	
394	405	412	403	407
307	320	334	346	295

TABLE 18. Vibrational spectral data for the copper(II) ethylenediamine and N-substituted ethylenediamine complexes. Nujol. 700-300 cm^{-1}.

$[Cu(en)_2]Cl_2$	$[Cu(en)_2]Br_2$	$[Cu(en)Cl_2]$	$[Cu(en)Br_2]$
	687	683	673
664	649		
526	526	532	526
470	483	480	472
403	405	378	367
380			
$[Cu(DAP)_2]Cl_2$	$[Cu(DAP)_2]Br_2$	$[Cu(DAP)Cl_2]$	$[Cu(DAP)Br_2]$
			697
698	680	665	654
614	637	620	615
507	500	504	498
412	406	418	413
370	361	342	338
$[Cu(NNMe)_2]Cl_2$	$[Cu(NNMe)_2]Br_2$	$[Cu(NNMe)Cl_2]$	$[Cu(NNMe)Br_2]$
685	684	682	675
	656		
561	584	561	556
505	497	506	500
455	460	453	453
431	433	431	430
382	383	381	380
$[Cu(NN'Meen)_2]Cl_2$	$[Cu(NN'Meen)_2]Br_2$	$[Cu(NN'Meen)Cl_2]$	$[Cu(NN'Meen)Br_2]$
596	591	599	600
469	455	450	454
404	403	402	
379	374	357	353
$[Cu(NMeen)_2]Cl_2$	$[Cu(NMeen)_2]Br_2$	$[Cu(NMeen)Cl_2]$	$[Cu(NMeen)Br_2]$
		657	654
562	558	556	553
485	483	481	478
451	453	460	455
408	407	367	361
$[Cu(NEten)_2]Cl_2$	$[Cu(NEten)_2]Br_2$		$[Cu(NEten)Br_2]$
674	694		694
634			662
563	571		558
532	529		527
416	410		422
			390

TABLE 18 continued ....

$[Cu(NPren)_2]Cl_2$	$[Cu(NPren)_2]Br_2$	$[Cu(NPren)Br_2]$
(704)	694	675
		660
578	574	586
540	541	539
485	485	520
419	415	415
		393

(iii) Electronic Spectra.

TABLE 19. Ultraviolet-visible spectra of the trivalent transition metal tropolonates as solids on filter paper.

	λnm	λ(kK)	Assignment.
Sc T_3	374	26.7	$\pi \rightarrow \pi^*$
	327	30.6	$\pi \rightarrow \pi^*$
	242	41.3	$\pi \rightarrow \pi^*$
V T_3	418	23.9	$^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$
	383	26.1	
	360	27.8	$\pi \rightarrow \pi^*$
	318	31.5	$\pi \rightarrow \pi^*$
	240	41.7	$\pi \rightarrow \pi^*$
Cr T_3	605	16.5	$^4A_{2g} \rightarrow {}^2E_g$
	556	18.0	$^4A_{2g} \rightarrow {}^4T_{2g}$
	396	25.3	$\pi \rightarrow \pi^*$
	334	29.9	$\pi \rightarrow \pi^*$
	246	40.7	$\pi \rightarrow \pi^*$
Mn T_3	575	17.4 }	$^5E_g \rightarrow {}^5T_{2g}$
	530	18.9 }	
	393	25.4	$\pi \rightarrow \pi^*$
	337	29.7	$\pi \rightarrow \pi^*$
	254	39.4	$\pi \rightarrow \pi^*$
Fe T_3	583	17.2	
	538	18.6	
	418	23.9	
	356	28.1	$\pi \rightarrow \pi^*$
	325	30.8	$\pi \rightarrow \pi^*$
	243	41.1	$\pi \rightarrow \pi^*$
Co T_3	610	16.4	$^1A_{1g} \rightarrow {}^1T_{1g}$
	386	25.9	$\pi \rightarrow \pi^*$
	343	29.2	$\pi \rightarrow \pi^*$
	247	40.5	$\pi \rightarrow \pi^*$

III. DISCUSSION.

1. VIBRATIONAL SPECTRA OF TRANSITION METAL TROPOLONATES.

(i) Crystal Field Aspects of the Vibrational Spectra of the First Transition Series Di- and Trivalent Metal Ions.

It has been established that the metal sensitive frequencies (νM-O) of several series of transition metal complexes of β-ketoenolates and nitrogen donors exhibit a correlation with d orbital population, which is consistent with the relative CFSE's of the metal ions[3]. The order of dependence of νM-O on CFSE is given by Sc<Ti<V<Cr>Mn>Fe<Co>Ga for the trivalent metal ions and by Ca<Mn<Co<Ni>Cu>Zn for the divalent metal ions. There are two possible deviations from this predicted order, namely Cr>Mn and Ni>Cu, where Jahn-Teller distortion is possible. The CFSE for the metal tropolonate complexes may be calculated from the relationship (See Section I.1)

$$CFSE = -(0.4n_t - 0.6n_e)\delta g \qquad (3)$$

The value of δ is unknown for tropolone, but its precise value is not of consequence since it is a constant for the series and the CFSE's given in Table 20 are therefore expressed in terms of δ.

A knowledge of the structure and spin states, especially for complexes with d^4 - d^7 configurations, is necessary for calculating CFSE. The magnetic moments of the metal tropolonates indicate that the trivalent complexes are all high spin, except for Co(III) which is low spin, conforming with the findings for the β-ketoenolates.

FeT_3 has been found crystallographically to be octahedral[22] and it is assumed that the other tris complexes will also be octahedral.

The divalent complexes are all high spin. It has been suggested, on the basis of their intractability, that MnT_2, CoT_2 and NiT_2 are probably oligomerized, the MT_2 units being held together by trivalent oxygen atoms[11,50].

TABLE 20. CFSE data for metal tropolonates.

Complex	Config.	μ eff (B.M.)	g (kK)	-CFSE		$(\nu-\nu_0)$¶ (cm^{-1}) (1)	(2)	(3)	(4)	(5)	(6)
CaT_2	d^0	-	-	0	0	0	0	0	0	0	-
MnT_2	d^5	5.89	8.5	0	0	0	0	0	0	0	-
CoT_2	d^7	4.41	9.3	8Dq*	7.44δ*	0	4	7	1	0	-
NiT_2	d^8	2.94	8.9	12Dq*	10.68δ*	5	22	18	9	9	-
CuT_2	d^9	1.86	12.0	6Dq†	7.20δ†	16	49	59	8	23	-
ZnT_2	d^{10}	-	-	0	0	0	0	0	0	0	-
ScT_3	d^0	-	-	0	0	0	0	0	0	0	-
TiT_3	d^1	-	20.3	4Dq	8.12δ	7	11	-5	11	-8	-
VT_3	d^2	-	18.6	8Dq	14.68δ	20	34	9	0	6	-
CrT_3	d^3	3.79	17.0	12Dq	20.40δ	10	37	15	10	25	-
MnT_3	d^4	4.74	21.0	6Dq†	12.60δ†	-3	10§	3‖	8	17	-
FeT_3	d^5	5.78	14.0	0	0	0	0	0	0	0	0
CoT_3	d^6	0	19.0	24Dq‡	45.60δ‡	16	60	25	33	1	50
GaT_3	d^{10}	-	-	0	0	0	0	0	0	0	0

*Assuming octahedral coordination.

†Excluding Jahn-Teller stabilization.

‡Excluding the pairing energy.

§Taking νMn-O as mean of doublet at 611 and 592 cm^{-1}.

‖Taking νMn-O as mean of doublet at 583 and 528 cm^{-1}.

¶Graphically determined; the band identification numbers refer to [^{18}O] labelling of CuT_2[21].

Thus they probably resemble the polymeric octahedral structure of the $Ni(AA)_2$ trimer. A claim that high-spin CoT_2 is a planar complex[51] probably should be abandoned inasmuch as the similarity of its magnetic and spectral properties to those of associated $Co(AA)_2$ suggests an oligomerized structure involving octahedral cobalt(II) for this complex as well[50]. ZnT_2 can be either monomeric tetrahedral or polymeric octahedral as is $[Zn(AA)_2]_n$[52]. CuT_2 has a square planar structure which has been established by crystallographic measurements[23,24] and confirmed with EPR spectral measurements of CuT_2 and its chloroform adduct in glasses[53].

Although the vibrational spectrum of tropolone has been widely studied[17-21] the spectra of its metal complexes have received little attention. Ikegami has proposed assignments for the majority of ligand bands based partially on their solvent dependence[17-19]. More useful is the report by Junge in which the shifts induced by [^{18}O]-labelling of the ketoenol oxygen atoms of tropolone and its Cu(II) chelate were used to identify five possible (coupled) νCu-O bands in the range 750-400 cm^{-1}. The band patterns and frequencies in the mull spectra of the transition metal tropolonates are very similar above 750 cm^{-1} (see Fig. 1). Below 750 cm^{-1} the band positions are strongly sensitive to the coordinated metal ion. Five bands are found to exhibit a frequency variation with *d* orbital population of the metal ion which parallels the variation in the calculated CFSE values, except for the Cu(II) and Mn(III) complexes. The frequency trend is shown in Fig. 2 for the most sensitive band of each series. Fig. 2 is found to be similar to a

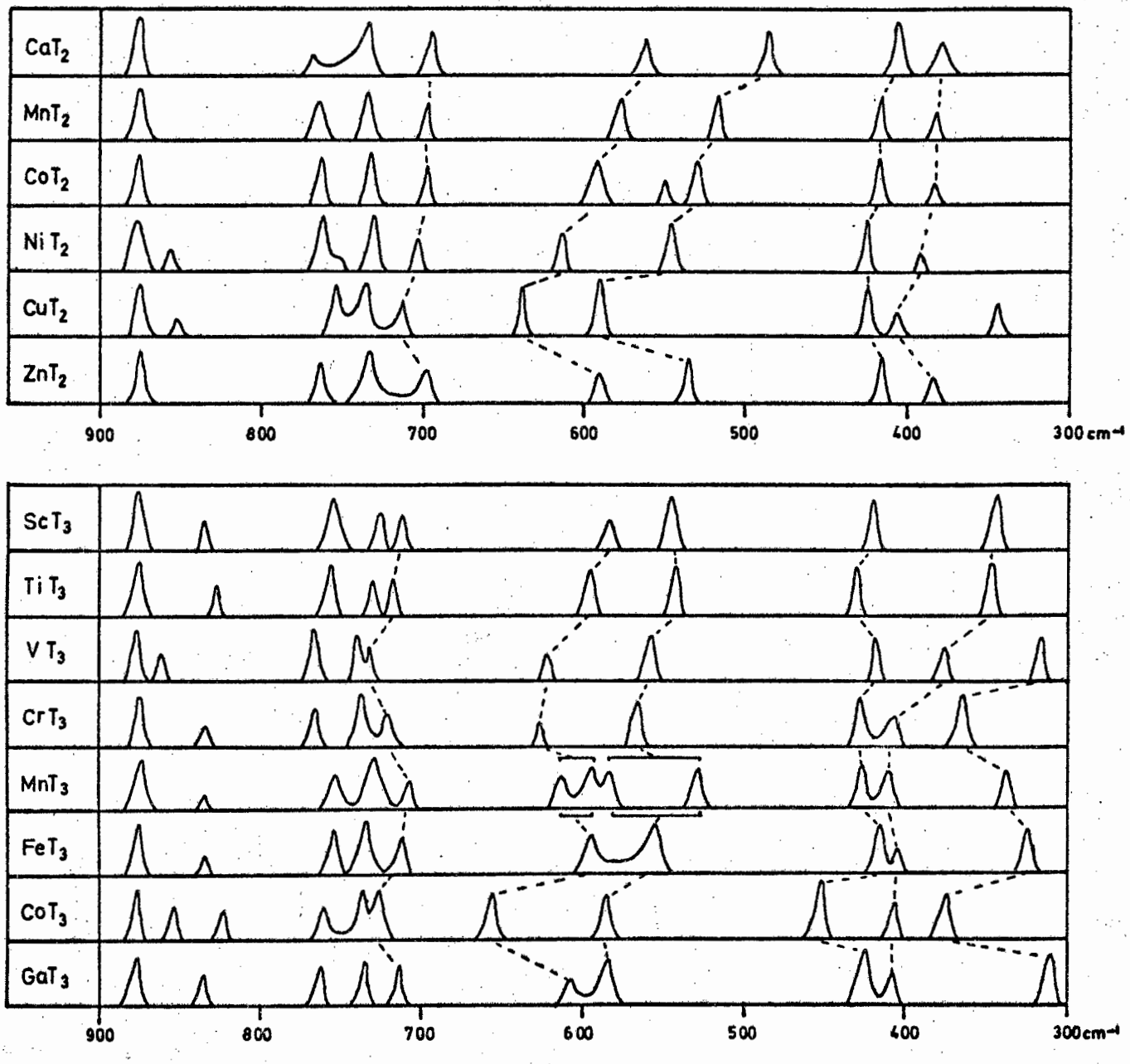


Fig.1. Vibrational spectra (900-300cm^{-1}) of di- and trivalent transition metal tropolonates.

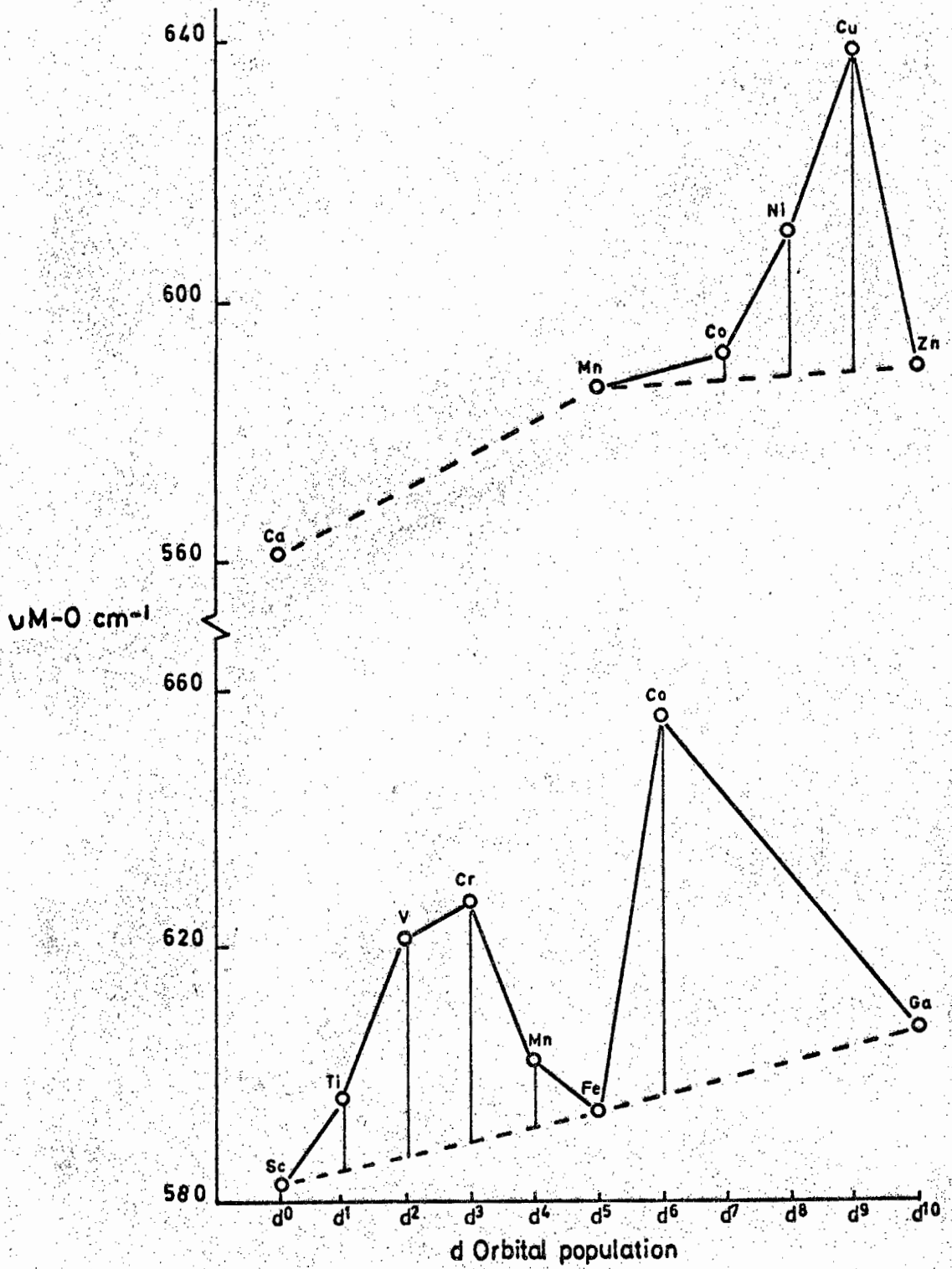


Fig. 2. Relationship between νM-O and d orbital population for di- and trivalent metal tropolonates.

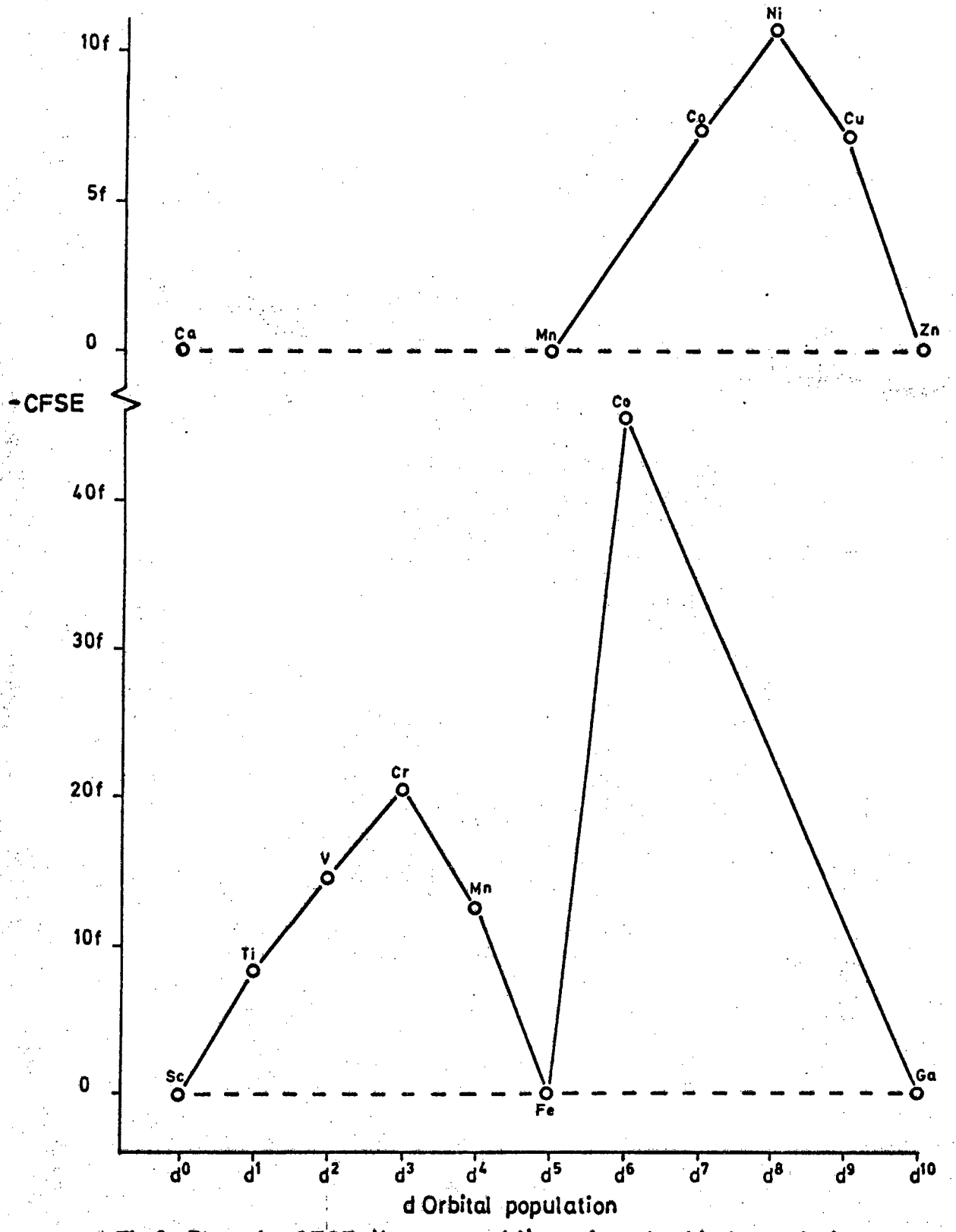


Fig.3. Plot of -CFSE (in terms of f) against d orbital population.

plot of CFSE (in terms of δ) plotted against atomic number (Fig. 3). This trend is also similar to that already established for the metal sensitive bands of the metal β-ketoenolate complexes[3]. These bands can therefore be assigned to the metal sensitive vibrations of the metal tropolonate complexes.

The contribution to the observed frequency (ν) provided by the CFSE is the difference ($\nu-\nu_0$) between the observed frequency and the frequency which would be realized in the absence of CFSE (ν_0). The (ν_0) values are obtained by drawing an interpolation line (the dashed line in Fig. 2) through the observed frequencies for complexes of ions with zero CFSE, i.e. Ca, Mn and Zn in the metal(II) series and Sc, Fe and Ga in the metal(III) series. Graphically determined values of ($\nu-\nu_0$) are given in Table 20 and these generally exhibit a qualitative parallel with the CFSE variation. The complexes of the three ions in each series with zero CFSE generally exhibit an increase in νM-O in the order Ca(II)<Mn(II)<Zn(II) and Sc(III)<Fe(III)<Ga(III). This is the order expected from the contraction of the ionic radii through the transition series but the opposite of that expected from their relative ionic masses. Clearly the former outweighs the latter in determining the frequency order.

These results correspond with those of George and McClure[2] for the variation of thermodynamic parameters with atomic number through a transition series. The slope of the interpolation line (ν_0) corresponds with $-E_r$, which is the contribution of the ionic contraction to the thermodynamic parameters. The deviations from this interpolation

line ($\nu-\nu_0$), correspond with $-\delta H$, which is the CFSE contribution to the total energy stabilizing the complex.

[^{18}O]-Labelling of CuT_2[21] produces a shift to lower frequency of the same five bands below 750 cm^{-1} that are found to exhibit the expected CFSE order. Their frequencies (with the shift on [^{18}O]-labelling in parenthesis) are: 405(-5), 424(-6), 714(-14), 639(-21) and 589(-26) cm^{-1}. These bands are therefore assigned[21] to increasingly pure Cu-O stretching frequencies in the order given, although some may represent O-Cu-O bending frequencies and in no instance can coupling with some ligand vibration be discounted. The bands in the spectra of the metal(II) tropolonates which correspond with those given above for the Cu(II) chelate exhibit a similar order of sensitivity to the CFSE and are therefore similarly assigned. The greatest sensitivity, as shown by the magnitude of ($\nu-\nu_0$), corresponds with the largest shift on [^{18}O]-labelling of CuT_2. This substantiates the use of CF trends to assign metal sensitive vibrations.

In the metal(III) tropolonates, six bands below 750 cm^{-1} exhibit the metal ion dependence expected from their CFSE's (the lowest frequency band not being observed for ScT_3 and TiT_3). Their sensitivities to substitution of the metal ion are similar to the corresponding bands in the metal(II) series indicating that similar assignments are appropriate. In the absence of [^{18}O]-labelling studies on any metal(III) tropolonate, further independent assessment of the validity of these assignments is not possible.

The question arises as to the extent to which the CFSE approach may be useful in assigning bands other than those arising from metal-ligand vibrations. Certainly

some ligand vibrations are known[3] to parallel the CFSE variation while others exhibit an inverse trend when the metal ion is varied through a transition series. The shifts are, of course, generally smaller than those observed for νM-L. Caution must be exercised in making assignments on the nature of the trend in the ligand vibrations (i.e. whether it is parallel to, or the inverse of, the CFSE order). It is well known[54] that in metal carbonyls there is almost invariably an inverse relationship between νM-C and νC-O : any change in the molecule which raises one frequency decreases the other. In metal hydrazine complexes, however, a simultaneous increase in νM-N and νN-N is observed on changing the coordinated ion[55]. The same is true of νM-O and νC-O in metal β-ketoenolates, both frequencies exhibiting a parallel trend with CFSE[3].

In the metal(II) tropolonates, no bands above 750 cm^{-1} exhibit any significant metal sensitivity. In the metal(III) complexes only the bands in the range 1300-1360 cm^{-1} exhibit any significant metal sensitivity and their frequencies are roughly the inverse of the CFSE order. The corresponding band in CuT_2 is also the only ligand band significantly shifted by [^{18}O]-labelling and hence assigned to (coupled)νC-O[21]. If this assignment is correct then the tropolonates differ from the β-ketoenolate complexes in that there is approximate constancy of bond order summation about the oxygen atom in the former but not in the latter. Structural determinations of the tropolonate[23,24] and acetylacetonate[56] of Cu(II) reveal a significantly greater C-O distance for the tropolonate, which is consistent with its considerably lower value of

νC-O. Assignment of the 1347 cm^{-1} band in CuT_2 to νC-O is therefore probably correct.

(ii) The Effect of Spin State on the Vibrational Spectra of Trivalent Metal Ions.

It was noted in the previous section that CoT_3 has a low spin configuration. The high value of νM-O for CoT_3 is associated with this configuration, all the other ions of the trivalent complexes having high spin.

In order to consider the effect of spin state on the CFSE and hence νM-O, it is necessary to include a further term to equation (3), thus

$$CFSE = -(0.4n_t - 0.6n_e)\Delta g + P \qquad (7)$$

The new term is the pairing energy P which is the total energy of the interelectronic repulsions of the electrons paired in orbitals, in low spin ions. Spin-paired states occur only in ions for which the increase in CFSE (relative to the spin free state) on spin-pairing, is greater than the pairing energy P. The large pairing energy pertaining to d^4 and d^5 ions of the first transition series accounts for the high spin states of Mn(III) and Fe(III) in most of their complexes. However the d^6 ions have a much lower pairing energy and it is thus possible for them to attain low spin configurations. The pairing energy for d^6 ions is given[2] by the relationship

$$P = 5B + 8C \qquad (8)$$

where B and C are the Racah interelectronic repulsion parameters. Values for the Racah parameters are reported[57] for the Co(III) ion (B = 1065 cm^{-1} and C = 5120 cm^{-1}) in the gaseous state. Using these values the total pairing

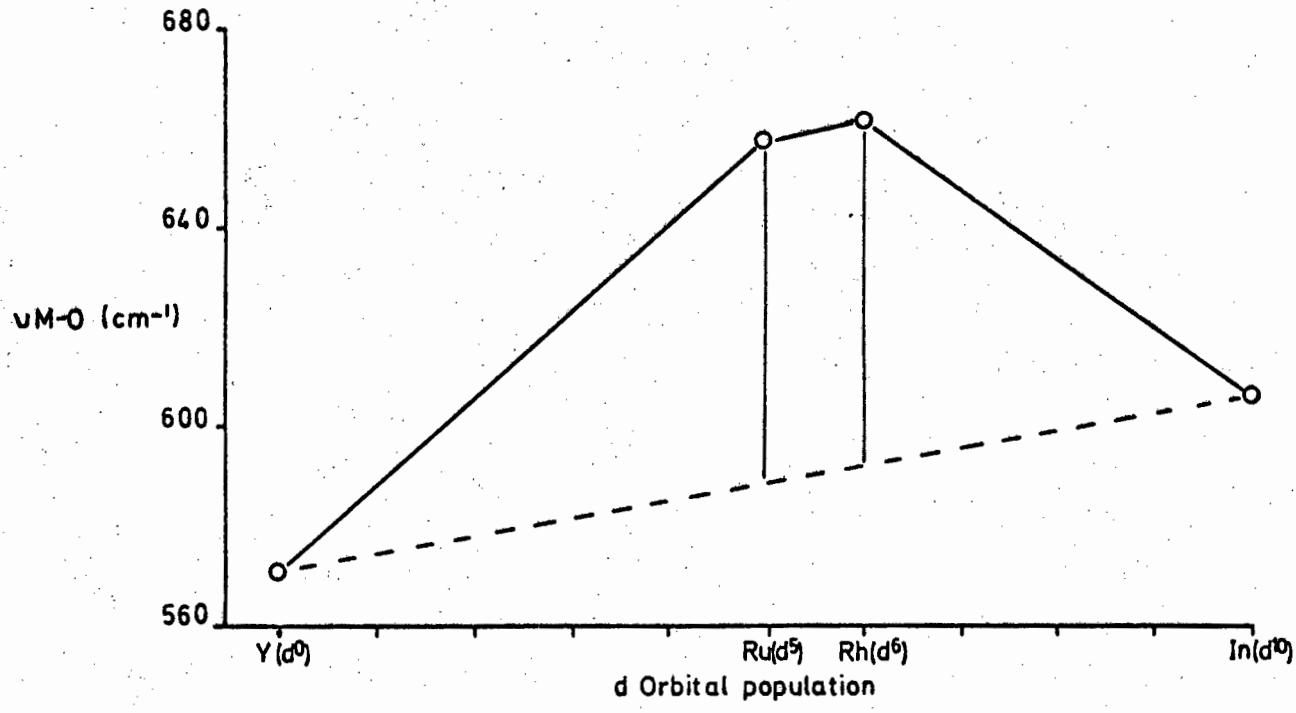


Fig. 5. Relationship between νM-O and d orbital population for second transition series metal tropolonates.

against atomic number for the peak in the 550-600 cm^{-1} range is shown in Fig. 5. From Fig. 5 it can be seen that νM-O follows the predicted trend for low spin ions. RuT_3 does not have zero CFSE like its first transition series analogue FeT_3, and its vibrational frequencies are similar to those of RhT_3. The interpolation line for ions with zero CFSE is drawn between YT_3 (d^0) and InT_3 (d^{10}). The values of $(\nu-\nu_0)$ for RuT_3 and RhT_3 are shown in Table 21 and are comparable as both are low spin complexes. This contrasts with the corresponding values for the vibrational spectra of FeT_3 and CoT_3. FeT_3 is high spin and lies on the interpolation line joining ions with zero CFSE, while CoT_3 is low spin and has a comparatively large CFSE.

Comparison of the data for the isoelectronic 3*d* and 4*d* complexes shows that the effect of spin pairing for the d^5 configuration (proceeding from high spin FeT_3 to low spin RuT_3) produces a large increase in νM-O. For the d^6 configuration, where there is no change in spin state, (both CoT_3 and RhT_3 are spin paired) the increase in νM-O is small. Thus the change in νM-O is observed to be large where the electron configuration changes to give a different value for the CFSE, but the change in νM-O is small where no change in electron configuration (and thus spin state) takes place.

TABLE 21. CFSE data for second transition series metal tropolonates.

Complex	Electron configuration	- CFSE	$(\nu-\nu_0)$ (cm^{-1})					
			1	2	3	4	5	6
YT_3	d^0	0	0	0	0	0	0	0
RuT_3	$d^5(t_{2g}^5)$	20Dq - P	-	69	42	23	-	-
RhT_3	$d^6(t_{2g}^6)$	24Dq - P	-	71	48	26	-	-
InT_3	$d^{10}(t_{2g}^6e_g^4)$	0	0	0	0	0	0	0
FeT_3	$d^5(t_{2g}^3e_g^2)$	0	0	0	0	0	0	0
CoT_3	$d^6(t_{2g}^6)$	24Dq - P	16	60	25	31	1	50

(iii) The Influence of Jahn-Teller Distortion on the Vibrational Spectra of Metal Tropolonates.

The complexes of the two ions for which strong Jahn-Teller distortion is possible, namely Cu(II) and Mn(III) are also the only examples which exhibit significant deviation of νM-O from the values expected from their CFSE calculated in the absence of the additional stabilization accompanying distortion.

The electronic spectrum of MnT_3[38] yields evidence for tetragonal distortion. The vibrational spectrum of MnT_3 is unique among the spectra of the MT_3 complexes (Fig. 1) in exhibiting four bands between 700 and 500 cm^{-1}, where two bands are normally observed. It seems clear that splitting arises from the existence of some distortion, probably resulting in four short and two long Mn-O bonds in the compound (assuming the distortion to be of the type usually observed, namely compression of the four coplanar metal-oxygen bonds).

That the tetragonal distortion of MnT_3 is not large is suggested by the $(\nu-\nu_0)$ values which are generally between those for CrT_3 and FeT_3, as would be expected in the absence of distortion. This agrees with the results observed[3] for $[Mn(AA)_3]$. X-ray diffraction studies of this molecule[59] show that the Mn-O bond lengths differ by 0.07 Å, which constitutes a relatively small distortion. However a marked splitting of the metal sensitive bands is observed, the split bands being between those observed for $[Cr(AA)_3]$ and $[Fe(AA)_3]$.

The crystal structure of CuT_2[23,24] shows that the molecule is very nearly planar (the plane of the Cu and O atoms makes an angle of 4.9^{o} with the plane of the C atoms). If planar coordination is regarded as an extreme case of Jahn-Teller distortion, the additional stabilization should be reflected by an exceptionally high Cu-O stretching frequency. Accordingly, the metal sensitive bands below 750 cm^{-1} for MT_2 complexes are found to exhibit a maximum frequency for CuT_2.

The distortion in MnT_3 is small, while the distortion of the CuT_2 is large, the tetragonal distortion being at its extreme (square planar). It has been established[60] for tris complexes of Cu(II) with ethylenediamine, 2,2'-bipyridine and 1,10-phenanthroline that in octahedral systems, rigid bidentate ligands offer a considerable resistance to the distorting forces. Thus in MnT_3 the tropolone ligand, being a reasonably rigid ring system, will tend to oppose the distorting forces accounting for the relatively small splitting of the vibrational bands. Divalent Cu(II) has only two ligands bound to it and the molecule readily distorts into a square planar structure which has a favourable (strong) tetragonal field stabilization. The strong distorting force in CuT_2 gives rise to a difference in structure between it and the other MT_2 complexes (square planar opposed to polymeric octahedral). This change in structure might also lead to the relatively high νM-O of the CuT_2 complex.

(iv) Vibrational Spectra of Adducts of Nickel and Zinc Tropolonate.

It has been previously suggested that the divalent metal tropolonates have polymeric octahedral structures, on the basis of their intractability. By studying the vibrational spectra of the adducts of these complexes, some further insight might be obtained as to their structures. The base adducts, $[MT_2B_2]$. yield reference 6-coordinate complexes for comparison with the spectra of the anhydrous tropolonates.

Only nickel tropolonate, of all the divalent metal tropolonates, forms a dihydrate. All the other divalent metal ions react with tropolone to form anhydrous complexes. Anhydrous NiT_2 can only be formed by sublimation of the dihydrate. For this reason the dihydrate of NiT_2 and the pyridine adduct were studied. Also the pyridine adduct of ZnT_2 as only one pyridine is adducted and the complex is 5-coordinate.

The spectra of nickel tropolonate and its two adducts (Fig. 6) exhibit (apart from the pyridine vibrational bands) identical band patterns. This feature of itself implies octahedral coordination in the anhydrous complex. Assumption of 4-coordinate Ni(II) in the anhydrous tropolonate would imply an increase in coordination number on proceeding to the dihydrated complex. In the absence of any change in ligand composition, increased coordination number leads to a considerable shift to low frequency of the metal sensitive vibrations. The coordination between the metal and the ligands is distributed over more metal-ligand bonds and this leads to a weakening of these bonds. Subsequently

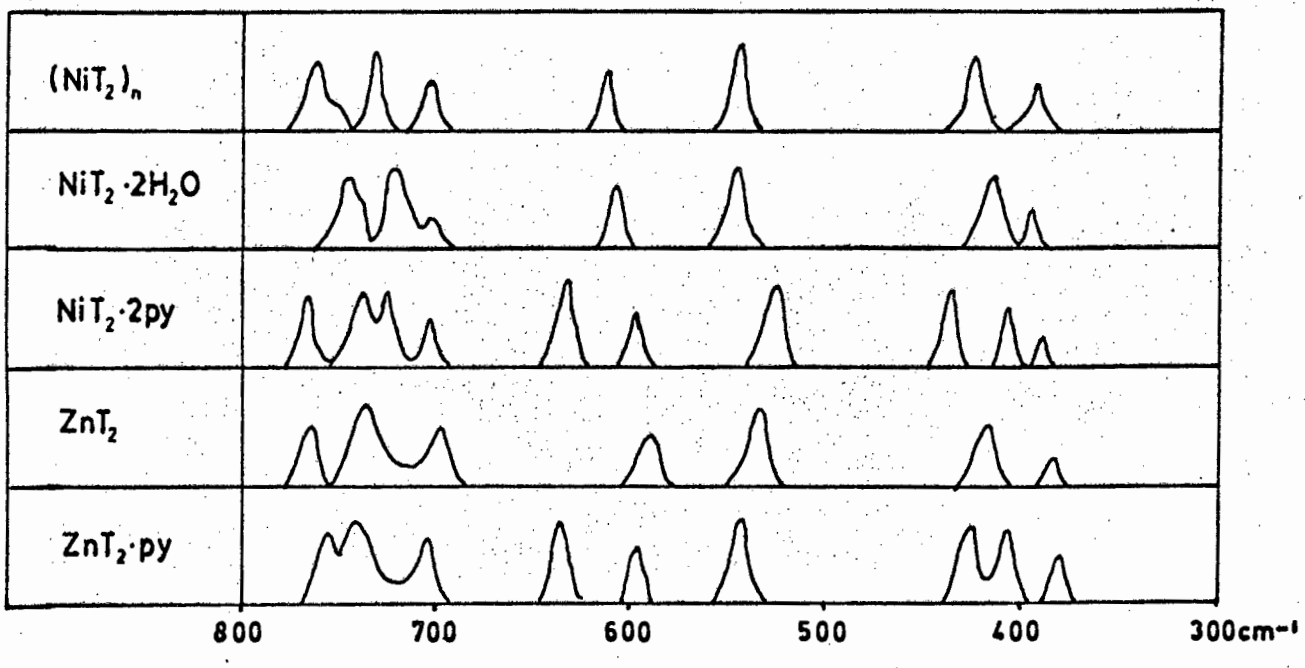


Fig.6. Vibrational spectra (800 -300cm^{-1}) of some divalent metal tropolonates and their adducts.

a decrease in the metal sensitive vibrations, associated with these bonds, occurs. The transformation from the anhydrous NiT_2 to the hydrated $[NiT_2 \cdot 2H_2O]$ involves replacement of tropolonate anion by water which has a slightly lower CF splitting strength (H_2O is lower than tropolone in the spectrochemical series). It is known[61] that a decrease in the CF splitting strength of an adducted base in metal acetylacetonates leads to an increase in νM-O. Assuming this to hold for the tropolonates also, a small increase in νNi-O is expected to accompany a transfer to the dihydrate adduct, from the anhydrous complex, if no change in coordination number is involved. The observed increase of 1 cm^{-1} in the vibrationally purest νNi-O band is therefore consistent with a 6-coordinate Ni(II) anhydrous complex.

Pyridine occurs higher in the spectrochemical series than tropolone and water (pyridine has a greater CF splitting strength). Therefore some reduction in νNi-O is expected to accompany the transformation from anhydrous NiT_2 to the adduct $[NiT_2py_2]$ even assuming 6-coordination in both complexes. The observed decrease of 17 cm^{-1} for the most metal sensitive band, is identical with that observed[61] in the transformation of anhydrous $[Ni(AA)_2]_3$ to $[Ni(AA)_2py_2]$ where the Ni(II) complex is known[52] to be trimeric.

The d^{10} configuration of Zn(II) implies that no one stereochemistry is favoured relative to another on the basis of CF effects. In practice, ZnT_2 forms a 5-coordinate mono(pyridine) adduct. The main influence on νZn-O in the transformation from anhydrous ZnT_2 to $[ZnT_2py]$ will be a

change in coordination number. An increase in νZn-O is expected if $[ZnT_2]_n$ is 6-coordinate polymeric octahedral (n>1) and a decrease if ZnT_2 is 4-coordinate tetrahedral. The observed increase of 10 cm^{-1} in the vibrationally purest νZn-O band is consistent with polymeric octahedral coordination for the anhydrous $[ZnT_2]_n$(n>1).

(v) Octahedral Divalent Metal Tropolonates.

It has already been shown that in the case of MnT_3 the rigid chelate structure opposes any distorting forces, similar to the effect observed for the octahedrally bound tris copper complexes of 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen). In the case of $[Cu(phen)_3](ClO_4)_2$ the distorting force is estimated to be less than 5 kK[62].

It would be interesting to compare an octahedral copper complex of tropolone with CuT_2 where the distortion is strong and the molecule assumes a square planar structure. The bipy and phen adducts of the divalent metal tropolonates provide such a system. The adducted molecule is *cis*-coordinated and the three chelates (two tropolonate ions and one bipy or phen molecule) all have fairly rigid bites which could oppose any distorting forces.

The vibrational spectra of the complexes $[MT_2 \cdot bipy]$ and $[MT_2 \cdot phen]$ (M = Mn, Co, Ni, Cu and Zn) have two regions of interest (Fig. 7). Firstly, below 300 cm^{-1} one peak occurs which could be assigned to a metal-nitrogen vibration showing considerable metal sensitivity in the order of calculated CFSE's, namely Mn<Co<Ni>Zn. This band corresponds with that of maximum metal sensitivity (also in the order of calculated CFSE's) in the vibrational spectra[63] of

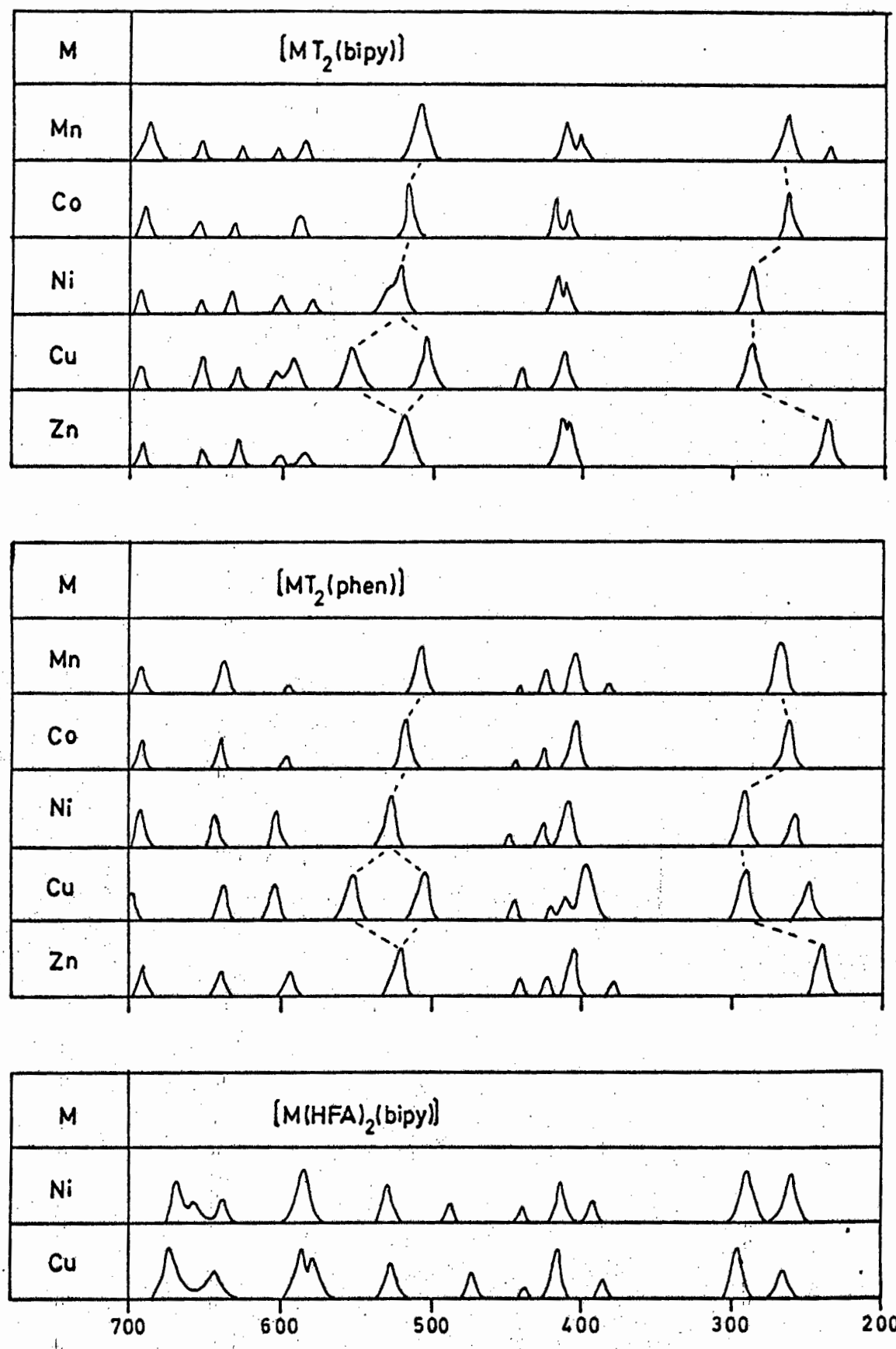


Fig.7. Vibrational spectra (700-200 cm-1) of bipy and phen adducts of divalent metal tropolonates.

$[M(bipy)_3](ClO_4)_2$ and $[M(phen)_3](ClO_4)_2$ and is therefore associated with a metal-nitrogen vibration (νM-N). Secondly, a number of peaks in the region 700-300 cm^{-1} having varying degrees of metal sensitivity in the order of calculated CFSE's. The majority of these peaks shift less than 10 cm^{-1} on changing the divalent metal ion through the whole range. The band in the 550-500 cm^{-1} range is the most metal sensitive. It corresponds to the most metal sensitive band observed for the divalent $[MT_2]_n$ complexes. It also corresponds to the 589 cm^{-1} band in CuT_2 which was shifted most on [^{18}O]-labelling. The band is thus associated with a metal-oxygen vibration (νM-O). The band is probably lowered from that observed in the $[MT_2]_n$ complexes due to the strong adduct bonds reducing the affinity of the metal ion for the tropolonate ligands.

Both νM-N and νM-O follow the expected CFSE order, except for νM-O of the Cu(II) complexes. νCu-O is split by 47 cm^{-1} for the bipy adduct and by 46 cm^{-1} for the phen adduct. The mean of the two bands give values which are approximately equal to that of the corresponding nickel complexes. Using this mean value for the Cu(II) complexes, the order for νM-O is Mn~Co<Ni~Cu>Zn which is similar to the order for νM-N.

For the calculated CFSE order to change from Ni>Cu (predicted by CFSE) to Ni<Cu (which is generally found for systems with distorted copper complexes) the stabilization energy associated with the distortion must be greater than the difference between the CFSE of the Ni(II) and Cu(II) complexes. In the case of the $[MT_2 \cdot bipy]$ and $[MT_2 \cdot phen]$ complexes, the CFSE can be calculated to

be 10.7δ kK for the [NiT_2·bipy] (or phen) and 7.2δ kK for the [CuT_2·bipy] (or phen). An approximate value of δ may be derived from the formula

$$\delta = \tfrac{1}{3}\,\delta(\text{bipy}) + \tfrac{2}{3}\,\delta\,(T) \qquad (10)$$

where δ(bipy) = δ(phen) = 1.48 and δ(T) is assumed to have a value similar to acetylacetone, namely δ = 1.2. This gives a value of δ = 1.28 and CFSE values of 13.7 kK and 9.2 kK for the Ni(II) and Cu(II) complexes respectively. Thus the difference in CFSE is of the order of 4.5 kK. As the frequencies of the Ni(II) and Cu(II) complexes have similar values, it seems likely that the stabilization energy associated with the distortion is approximately 5 kK. This compares favourably with the findings for $[Cu(bipy)_3]^{2+}$ where the stabilization associated with the distortion is calculated to be of the order of 5 kK[62].

A crystal structure[64] of the compound [$Cu(HFA)_2$bipy] (HFA = hexafluoroacetylacetone) shows that the molecule is distorted. A two fold axis passes through the bipy ligand, requiring the two Cu-N bonds to be identical. The two Cu-O bonds in the plane of the Cu and N atoms are slightly shorter than the Cu-N bonds (namely 1.967 Å). However, the axial Cu-O bonds, to the second oxygen of each HFA ring, are much longer (2.296 Å) producing the 'four short-two long' bond distortion of the octahedron.

The vibrational spectra of this complex and its Ni(II) analogue have been determined. The νM-N values for the Ni(II) and Cu(II) complexes are similar, occurring at 290 and 295 cm^{-1} respectively, the band retaining singlet character in the Cu(II) complex. The νM-O occurs at 589 cm^{-1} for the Ni(II) complex. This is at higher frequency

than found for the respective tropolone complex but is consistent with similar bands assigned for other fluoro-containing complexes, e.g. $K[Ni(TFA)_3]\cdot 2H_2O$ (TFA = trifluoroacetylacetone) νNi-O = 585 cm^{-1}[63]; $[Ni(TTA)_2(H_2O)_2]$ (TTA = thenoyltrifluoroacetone) νNi-O = 591 cm^{-1}[65]; $[Ni(TTA)_2]_n$ νNi-O = 592 cm^{-1}[65]. The corresponding band for the Cu(II) complex is the only band to be split into a doublet at 580 and 588 cm^{-1}. This supports the observations of the crystal structure which indicates that the Cu-N bonds are similar, but that the Cu-O bonds have two different bond lengths. A similar situation probably occurs in the adducts of the tropolonate complexes. The νCu-N shows no splitting, while νCu-O is split by 47 cm^{-1} suggesting that the distortion takes place through the Cu-O bonds and not the Cu-N bonds.

(vi) Vibrational Spectra of Divalent Metal 2-Thiotroponates.

Although there is not much reported work on metal complexes of 2-thiotropone (HST), sufficient is known of the structures of metal complexes with sulphur containing ligands[50,66-68] to enable some predictions to be made regarding their structures.

$Ni(ST)_2$ has been found to be monomeric and diamagnetic[11] suggesting that it is a four coordinate square planar complex (in keeping with its deep purple colour). All Ni(II) complexes with sulphur ligands are found to be diamagnetic and therefore square planar[69]. It is probable that the dark brown Cu(II) complex of 2-thiotropone is also square planar. The dithiotropolone complexes[70] of Ni(II) and Cu(II) are found to be planar, while the complex

of Zn(II) is tetrahedral. Zn(II) complexes of monothio-β-ketoenolates[50] are usually found to be tetrahedral, while of the four Co(II) complexes with monothio-β-ketoenolates[50] three have tetrahedral while one, namely $Co(SDPM)_2$ (SDPM = monothiodipivaloylmethane),is found to be planar. However dipivaloylmethane complexes are known to prefer square planar structures, an example being square planar $Ni(DPM)_2$[71]. Thus it is assumed that $Co(ST)_2$ and $Zn(ST)_2$ are tetrahedral.

The thiotropone complexes of the divalent metal ions therefore offer an example of Ni(II) and Cu(II) in an isostructural environment, with Cu(II) free from Jahn-Teller distortion. In previous cases the Cu(II) complexes have been distorted and had different structures to the analogous Ni(II) complexes. For square planar complexes with electron configurations d^8 - Ni(II) and d^9 - Cu(II) the ninth electron can only enter an orbital which has a destabilizing effect on the CFSE of the complex. Further, in a square planar environment, the *d* orbitals are split in such a manner that the degenerate orbital system which produces Jahn-Teller distortion does not exist. Thus $Cu(ST)_2$ does not have any added stability due to distortion and the CFSE order should be Ni>Cu and be shown by the metal sensitive bands of the vibrational spectra of these complexes.

The vibrational spectra of the metal(II) thiotropones have three sets of bands in the region below 700 cm^{-1} which show metal sensitivity (Fig. 8). The three sets of bands comprise a single band in the 450 cm^{-1} region, a single band in the 550 cm^{-1} region and two bands above 600 cm^{-1} ($Zn(ST)_2$ has only one band in this region, at 597 cm^{-1}). An unusual feature of the spectra is the absence of any bands below the

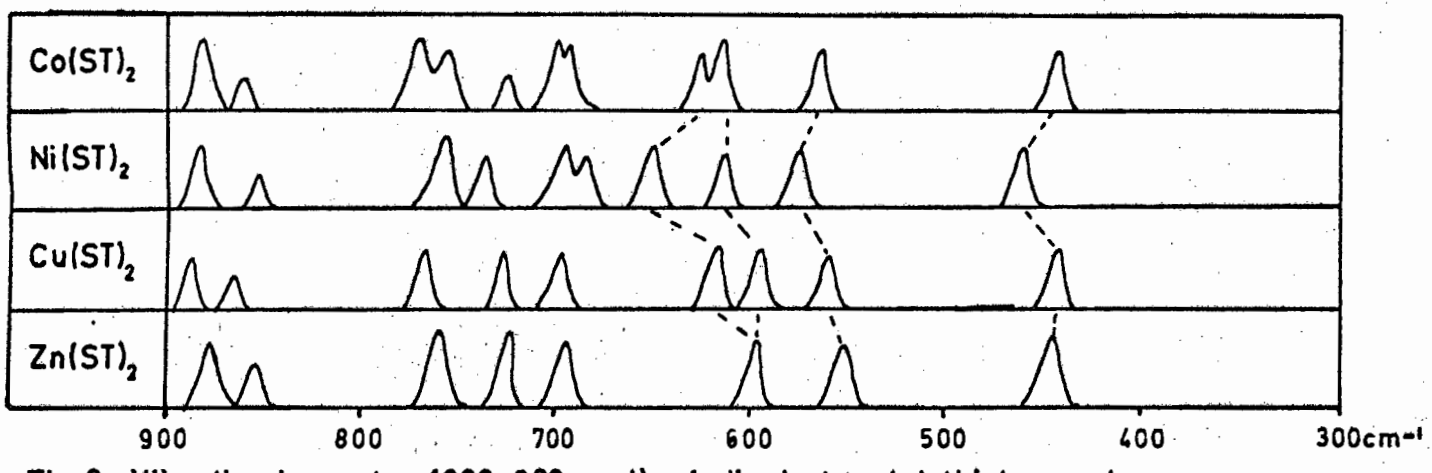


Fig. 8. Vibrational spectra (900-300cm^{-1}) of divalent metal thiotroponates.

450 cm^{-1} band, particularly as metal-sulphur vibrations are known to occur in the region below 400 cm^{-1}[72].

In all cases, the metal sensitive bands follow the order Co<Ni>Cu>Zn. This confirms the predicted CFSE order of Ni>Cu for square planar complexes where Jahn-Teller distortion is absent. If all the complexes were square planar, the order would be Co>Ni>Cu>Zn, so that the observed order confirms that $Co(ST)_2$ is not square planar and is probably tetrahedral. However the possibility of polymeric octahedral coordination does exist for both $Co(ST)_2$ and $Zn(ST)_2$.

Assuming that it is tetrahedral, it can be seen that the CFSE for square planar complexes is greater than the CFSE for tetrahedral (or possibly polymeric octahedral) complexes, as the order for tetrahedral complexes predicts Co>Ni.

2. CRYSTAL FIELD ASPECTS OF THE VIBRATIONAL SPECTRA OF LANTHANIDE(III) TROPOLONATES.

It has now been established that the variation in metal-ligand vibrational stretching frequencies, through a series of $3d$ transition metal ion complexes with constant ligand composition, may be rationalized in terms of CFT. The shift in νM-L with $3d$ orbital population is considered to be a function of the metal ion radius, the ionic mass and the CFSE. Since the first two of these effects exhibit a relatively smooth variation with atomic number, the shift in νM-L reflects the variation in CFSE.

In lanthanide complexes, CF effects are greatly reduced in significance[2] and cation size becomes the predominant feature determining complex stability. Although complexing groups have only a small effect on the permanent magnetic moments of the lanthanide(III) ions or upon the positions of the electronic absorption bands, George et al[73] have proposed that CF splitting of the $4f$ orbitals may be sufficient to influence the enthalpies of lanthanide complex formation. The vibrational spectra of a series of lanthanide complexes with constant ligand composition may therefore yield evidence in support of the presence of CF stabilization in lanthanide complexes.

In examining the dependence of thermodynamic parameters on $4f$ orbital population, a complication arises from the variable coordination number of the lanthanide(III) ions. This feature of their chemistry yields problems of variable solvation number (in solution measurements) and variable structure and composition (in solid state measure-

ments). For these reasons it is rarely possible to synthesize a complete series of lanthanide(III) complexes with identical structure and composition and such isostructural series as do exist are not necessarily suited to an investigation by vibrational spectroscopy in view of uncertainties which can arise from the assignment of metal sensitive bands. There is no report in the literature of a vibrational spectral study of a complete isostructural range of complexes with a common ligand, for all the accessible lanthanide(III) ions.

Tropolonate complexes of lanthanide(III) ions have been studied by Muetterties and Wright[9], who have synthesized several series of complexes of the type $[Ln(III)T_3]_n$, $Li[Ln(III)T_4]$ and $Na[Ln(III)T_4]$ (Ln(III) = lanthanide(III) ions). These series are therefore preparatively accessible and the empirical composition is identical within each of these series. Previous work on the $[^{18}O]$-labelling of CuT_2[21] has provided a basis for assigning the metal sensitive νLn-O. This is further substantiated by the work on the vibrational spectra of the divalent and trivalent 3*d* metal ion complexes, which have been interpretted in terms of CF theory. Campbell and Moeller[74,75] have published work on the stability constants and thermodynamically-derived enthalpy and entropy data, so that a parallel exists for a comparison of the vibrational spectral results.

The most important feature of the tropolonate complexes however, is their structures. All the complexes are anhydrous, eliminating problems of various solvation numbers which usually disrupt such studies. The $[Ln(III)T_4]^-$

ions are all isostructural and, although there is a structural transition in the series $[Ln(III)T_3]_n$, it is known that the insoluble tropolonates of the ions La(III) through to Ho(III) possess a polymeric lattice with co-ordination number exceeding six (and possibly eight or nine), while the last four members are structurally different, isomorphous and, by nature of their solubility in organic solvents, may have monomeric octahedral coordination (but certainly lower coordination than that found in the preceding complexes).

Yatsimirskii and Kostramina[76] have analysed the CF effects in complexes of $4f^n$ ions. The variation of the CFSE with $4f$ orbital population has the double-humped shape, characteristic of the CFSE's of octahedral $3d^n$ ion complexes, with minima at the $4f^0$, $4f^7$ $4f^{14}$ configurations which are not stabilized by the CF. Experimental support for the theoretical predictions that lanthanide(III) complexes are stabilized by the CFSE can at present only be sought in the broadest qualitative sense, since the CFSE is a function of the CF splitting, 10 Dq, and neither absolute or relative values of this parameter are currently available for lanthanide(III) complexes.

A relationship between log β_3, derived from previously determined stability constants[74] (see Table 22) and $4f$ orbital population is depicted in Fig. 9. The stabilities are observed to fall on a double-humped curve superimposed on an interpolation line of positive slope. Following the method proposed by George and McClure[2] for a CF interpretation of the stabilities of complexes of $3d$ metal ions, the interpolation line connecting the points

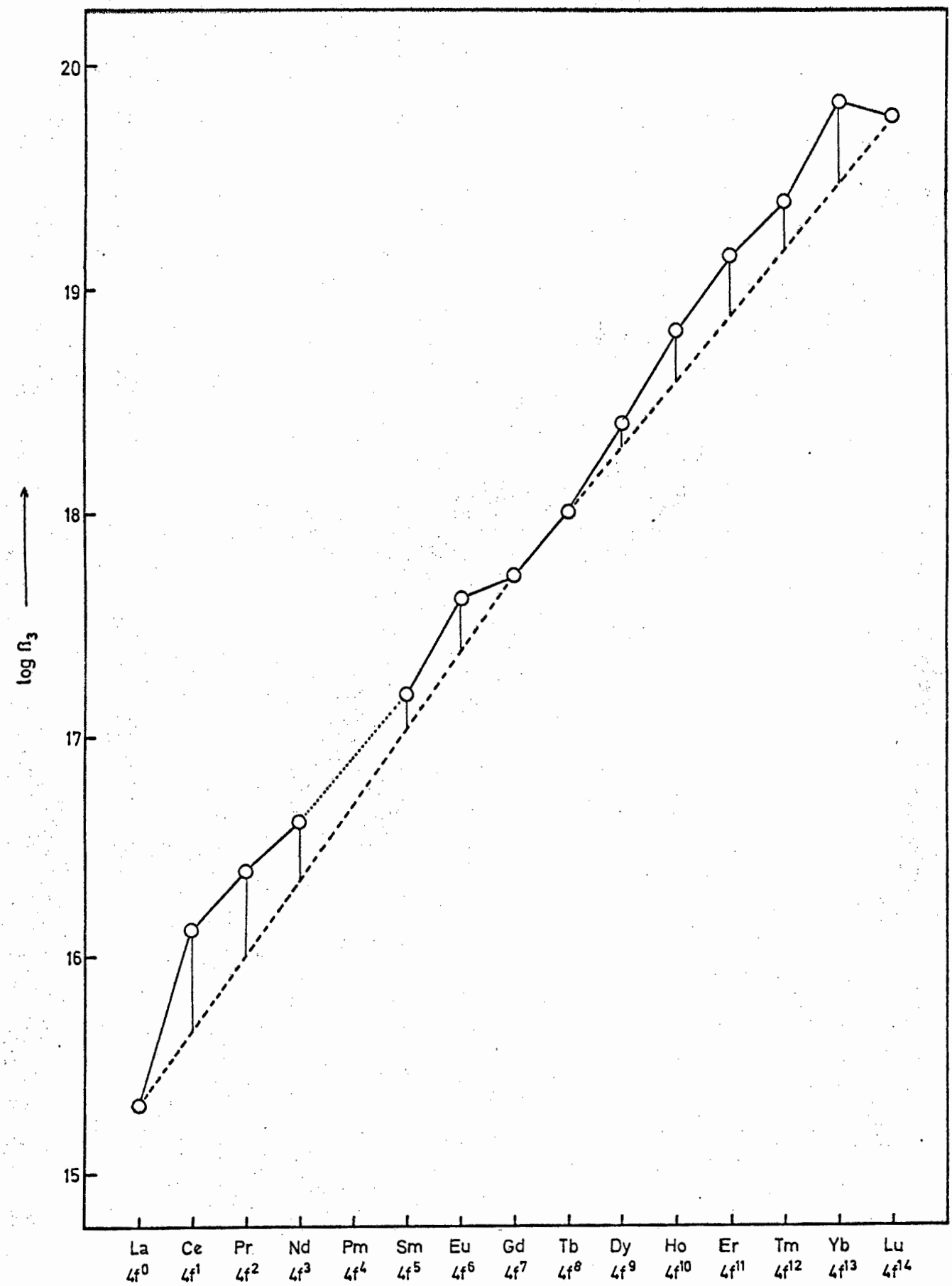


Fig.9. Relationship between log β_3 and 4f-orbital population for lanthanide tropolonates (data from ref. 74). The dashed line represents $(\log \beta_3)_0$ and the vertical lines represent $\delta(\log \beta_3)$.

$4f^0$, $4f^7$ and $4f^{14}$ complexes represents the stabilities, designated $(\log \beta_3)_0$, which arise from the lanthanide ion contraction. The differences, $\delta(\log \beta_3)$, between the observed stabilities and $(\log \beta_3)_0$, represent the contribution to $\log \beta_3$ provided by the CF stabilization. Of more fundamental importance than the stability effects, is the contributions of the enthalpy and entropy terms to the free energy relationship. It has been verified in certain cases (but more often tacitly assumed) that the entropy term is either approximately constant or varies smoothly with atomic number, through a series of $3d$ metal ion complexes with constant ligand composition. Such assumptions are less permissible for lanthanide complexes in view of the relative significance of the entropy contribution to the free energy.

Thermochemically-derived values of the 1:1 formation enthalpies (ΔH_1) and entropies (ΔS_1) have been obtained[75] for the lanthanide(III) tropolonate complexes. The insolubility of the tris tropolonates precludes their determination. The variations of ΔH_1 and ΔS_1 with $4f$ orbital population do not conform with the curves generally observed for the lanthanide complexes of other ligands. Whereas a discontinuity is usually observed in the middle of the series which is associated with some structural transition in the hydration sphere, this is not so for the tropolonates. The positive ΔS_1 values increase relatively smoothly through the series while the variation of ΔH_1, although small, approximates the double-humped curve associated with the presence of CF stabilization.

(i) Vibrational Spectra of the Tetrakis (tropolonato) Lanthanide(III) Complexes.

The lithium and sodium salts of the $[Ln(III)T_4]^-$ ions represent two similar series of compounds which appear to have isostructural character, from the patterns of their vibrational spectra. The lithium salts are a complete series of lanthanides, while the sodium salt of the lanthanum ion could not be synthesized[9]. This is significant as this compound has the $4f^0$ electron configuration which represents one of the zero CFSE states, for interpolation purposes. Although the spectra of the two series, $Li[Ln(III)T_4]$ and $Na[Ln(III)T_4]$ are similar, there are some recognizable differences, particularly the doublet character (in the sodium salts) of the band at 1240 cm^{-1} and the appearance of additional bands in the lithium salts near 770, 435, 360 and 340 cm^{-1}. This suggests that while there is undoubtedly structural identity within each series, the structures of the sodium and lithium salts may differ. This could possibly arise from different crystal packing, due to the different ionic radii of the sodium and lithium ions, giving rise to various distortions of the molecule, or possibly allowing different interactions to occur.

In both series, the band near 500 cm^{-1} is the most sensitive to lanthanide ion substitution (See Fig. 10). The equivalent band in the spectrum of CuT_2 is also that which exhibits maximum shift on $[^{18}O]$-labelling. The relationship between the frequency of this band and $4f$ orbital population (Fig. 11) reveals the double-humped curve, with minima at the $4f^0$, $4f^7$ and $4f^{14}$ configurations, which is expected to result from the presence of CF stabilization.

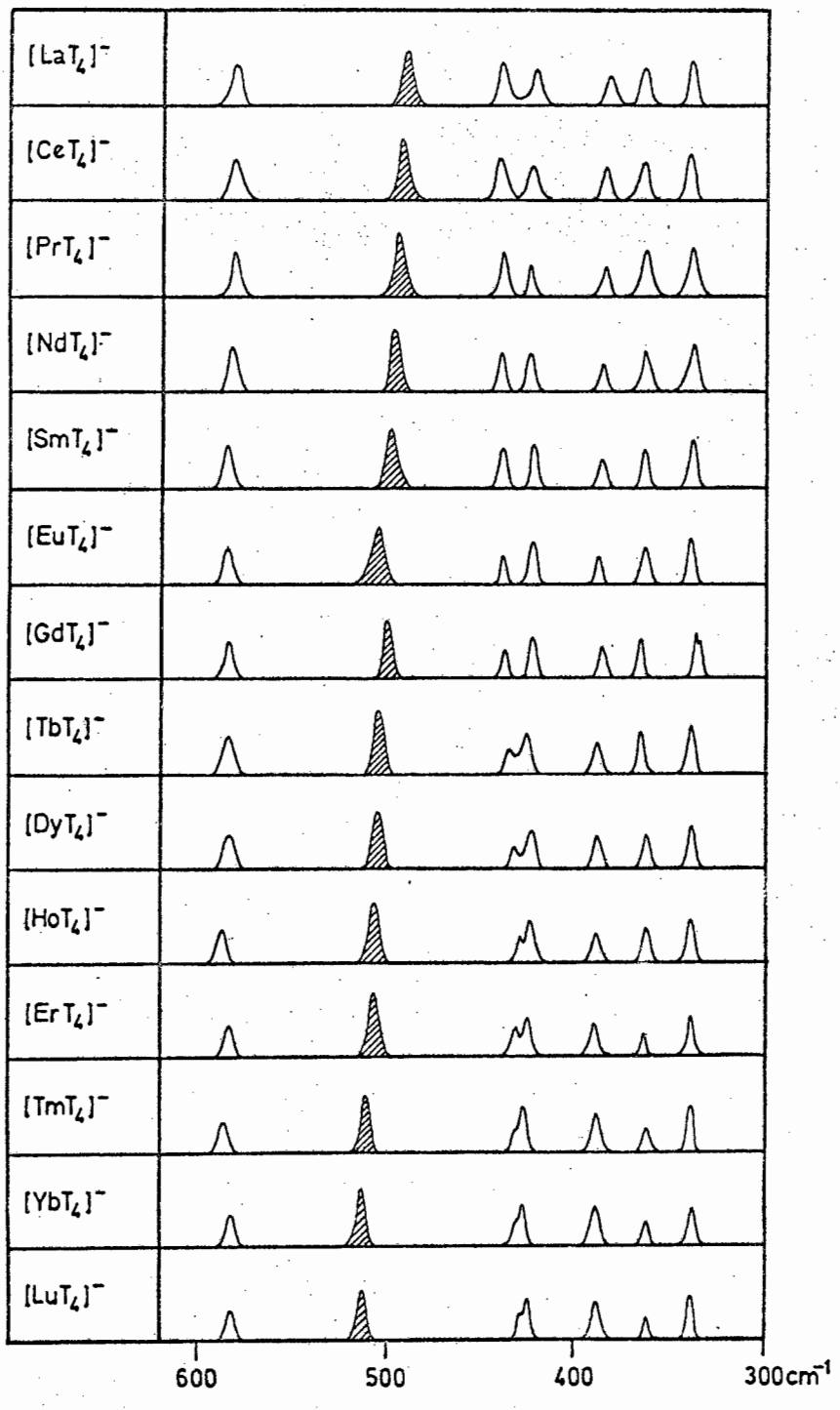


Fig.10. Vibrational spectra (600-300cm^{-1}) of tetrakis lanthanide tropolonate ions.

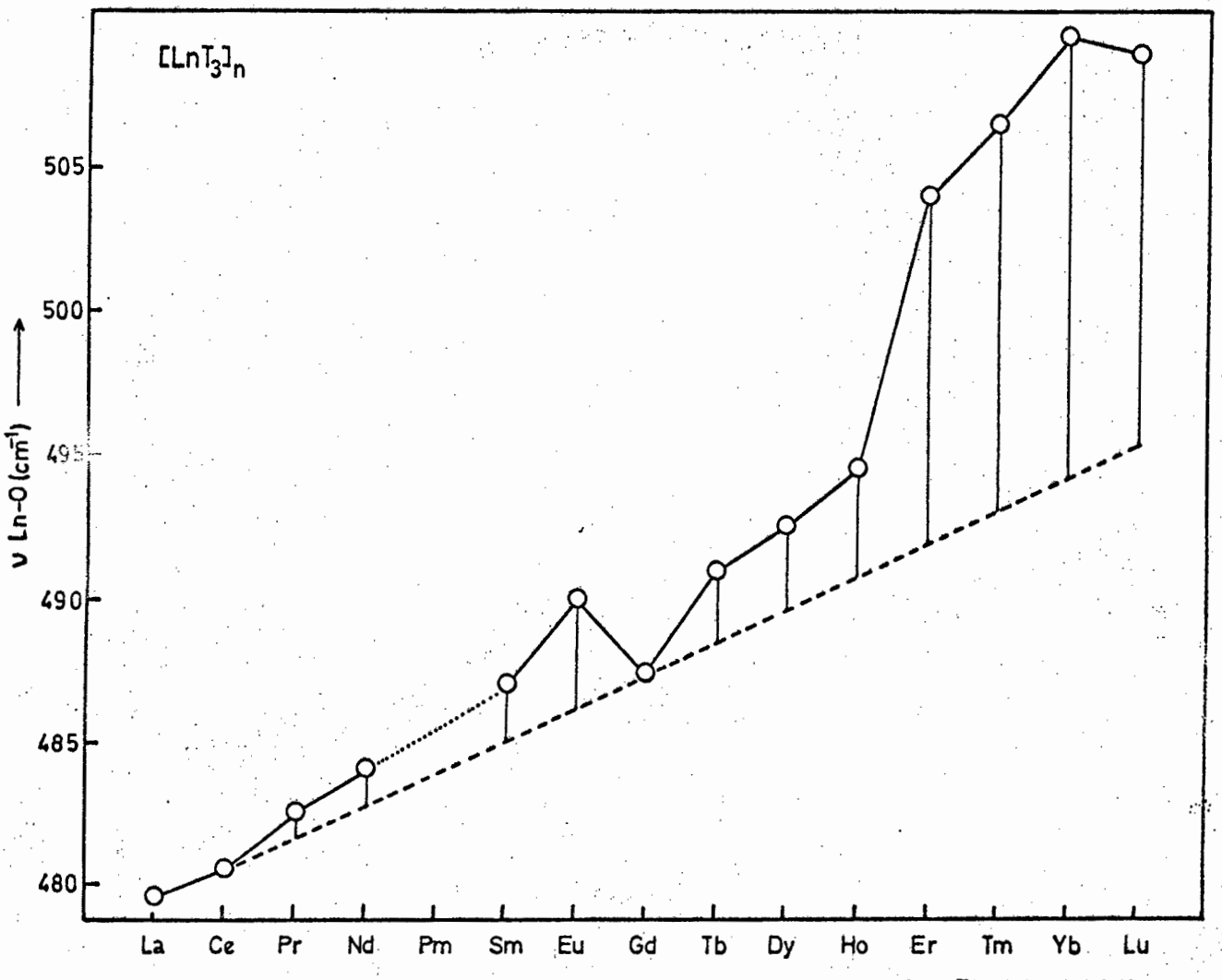


Fig.11. Relationship between υLn-O and 4f orbital population. The dashed lines represent υ_0 and the vertical lines represent $\delta(\upsilon$Ln-O).

In order to estimate the contribution of the CFSE to νLn-O, a similar procedure is adopted to that employed for the stability constants of the LnT_3 complexes, namely log β_3. The difference $(\nu-\nu_0)$ between the observed frequency and the frequency in the absence of CFSE, derived from the interpolation between $4f^0$ $4f^7$ and $4f^{14}$ configurations, represents the CF contribution to the stabilization of the complexes. That $(\nu-\nu_0)$ is very small compared with similar values for the *d* orbital metal ions, is in agreement with the earlier predictions from thermodynamic data, that the CFSE for *f* orbitals would be considerably smaller than for *d* orbitals.

An analysis of thermodynamic parameters for the lanthanide diglycollate and dipicolinate complexes[77,78] reveals that CF effects operate for the lanthanide ions on a scale between one and two factors of ten smaller than the effects for the 3*d* transition metals. A comparison of the vibrational spectra of the lanthanide complexes and the 3*d* transition metal tropolonates shows that $\delta(\nu$Ln-O) is approximately one twelfth that of $\delta(\nu$M-O), taking the most metal sensitive band in each case.

(ii) Vibrational Spectra of the Tris(tropolonato) Lanthanide(III) Complexes.

The vibrational spectra of LnT_3 are depicted in Fig. 12 which also includes the spectra of CuT_2 and ScT_3 for the purpose of assigning νLn-O. The six bands below 720 cm^{-1} in the spectra of CuT_2 and ScT_3 are all metal sensitive. Of the six bands below 720 cm^{-1} which are common to all the LnT_3 spectra, the four most intense bands are sensitive to substitution of the Ln(III) ion and are accordingly assigned

to coupled νLn-O. Of these four bands, the pair within the frequency ranges 558-575 cm^{-1} and 479-510 cm^{-1} exhibit the maximum metal sensitivity and are therefore considered to represent the vibrationally-purest νLn-O bands. This is in excellent agreement with the fact that the corresponding two bands in the CuT_2 spectrum are those which are shifted most towards lower frequency by [^{18}O]-labelling. Furthermore, the corresponding pair of bands in the ScT_3 spectrum are those which exhibit maximum sensitivity to substitution of Sc(III) by the remaining metal(III) ions of the 3*d* transition series.

The variation of the frequency of the vibrationally purest band (475-510 cm^{-1}) with $4f$ orbital population is shown in Fig. 13 (the less metal sensitive band at 558-575 cm^{-1} shows a similar trend). The most prominent feature of the relationship is the abrupt transition to higher frequency at the Er(III) complex. This is precisely the point at which a structural change is known to occur[9]. The associated reduction in coordination number serves to increase νLn-O since the bonding capacities of the Er(III) and succeeding Ln(III) ions are distributed over fewer metal-ligand bonds. If the non-monotonic variation of both νLn-O and log β_3 with $4f$ orbital population is ascribed to a common origin - the CF stabilization - then a simple relationship between νLn-O and log β_3 is expected, except for the $4f^{11}$ - $4f^{14}$ complexes which are structurally unique in the solid state. A linear relationship is observed between log β_3 and νLn-O, with the $4f^{11}$ - $4f^{14}$ complexes lying well off the curve (Fig. 14).

The LnT_3 complexes do not present an idealized series of lanthanide complexes, with $4f^0$, $4f^7$ and $4f^{14}$

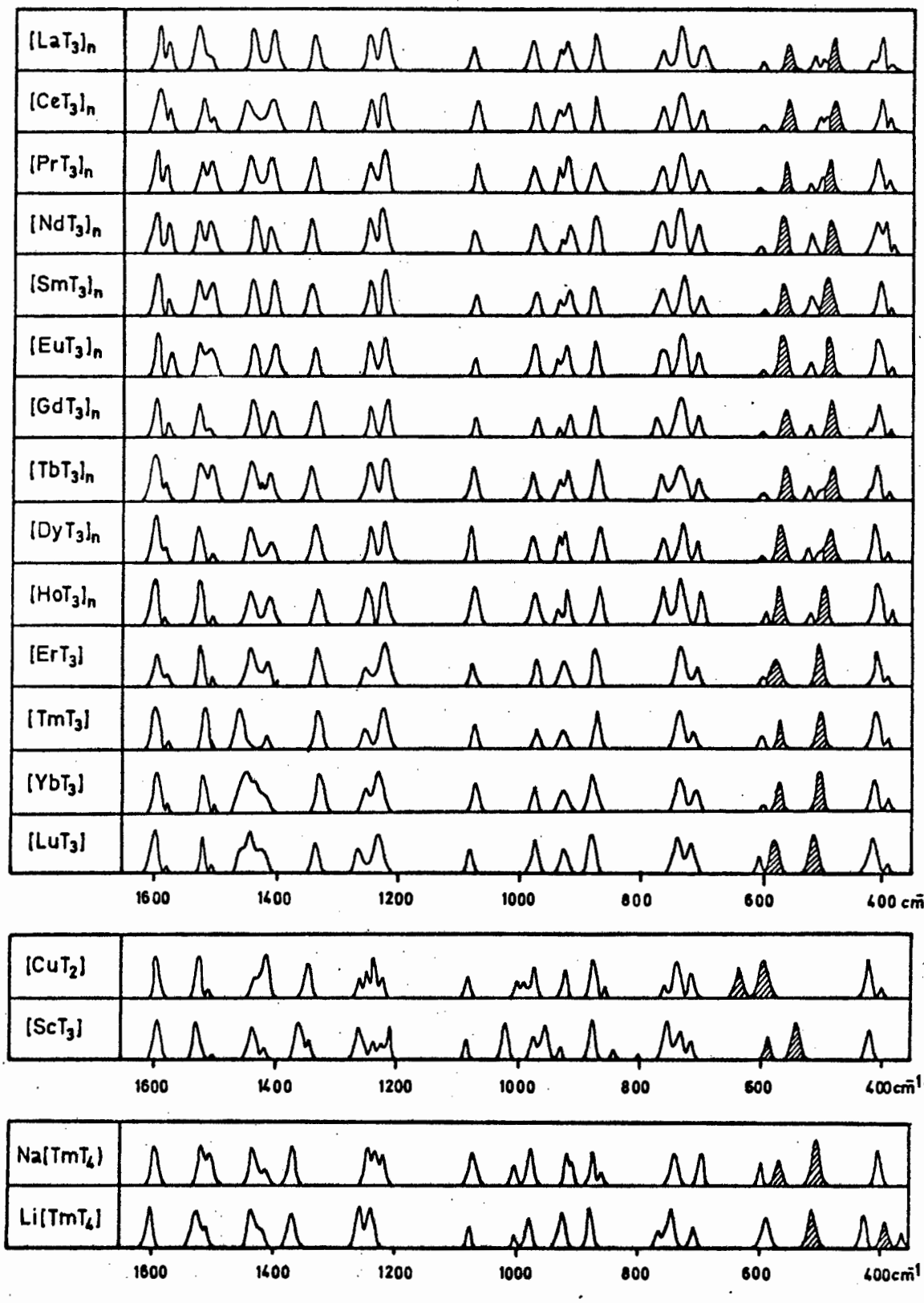


Fig.12. Vibrational spectra (1600 - 400 cm^{-1}) of the tris lanthanide tropolonates.

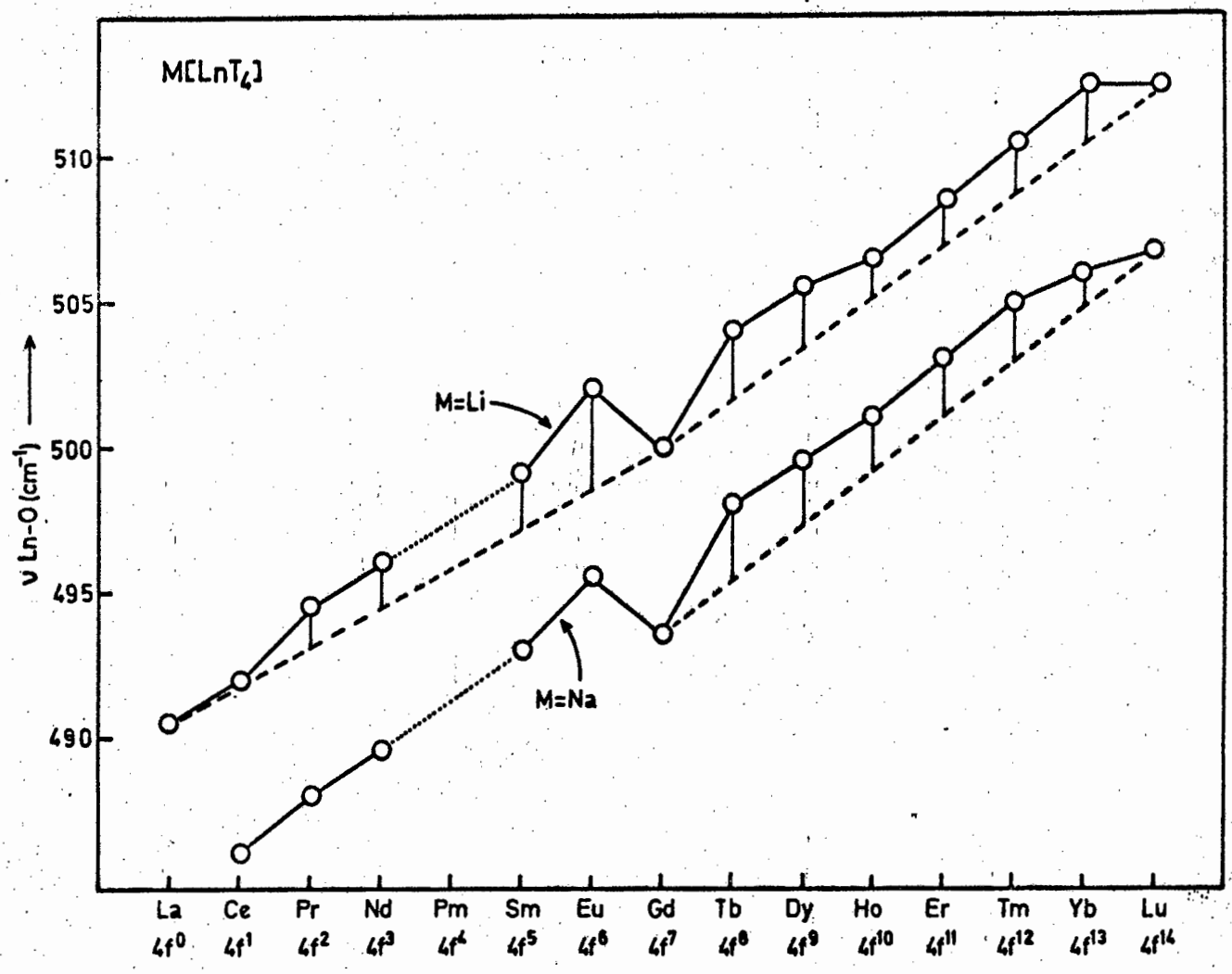


Fig.13. Relationship between νLn-O and 4f-orbital population. The dashed lines represent ν_0 and the vertical lines represent δ(νLn-O).

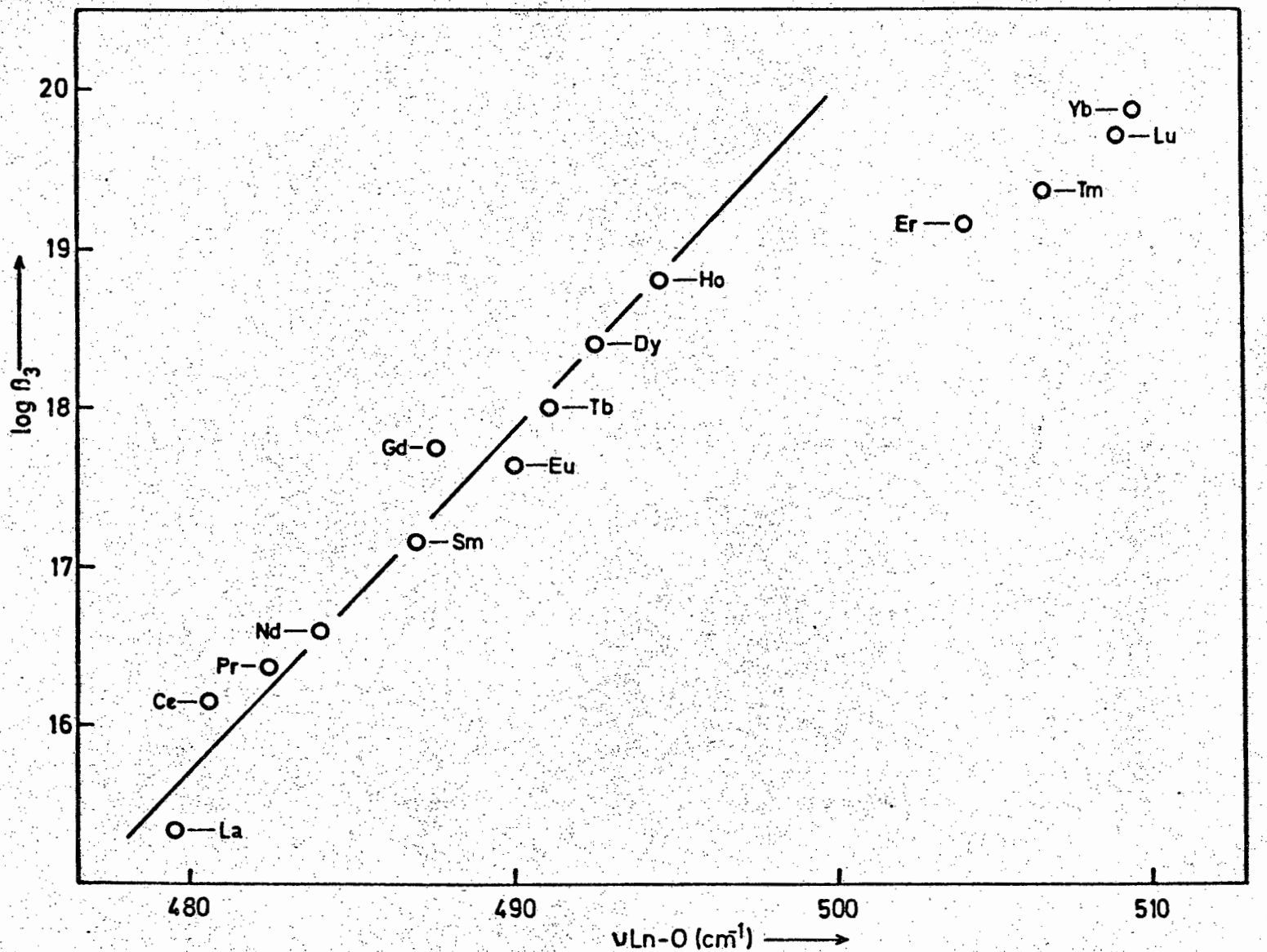


Fig.14. Relationship between $\log\beta_3$ and ν Ln-O for $[LnT_3]_n$ complexes.

configurations representing zero CFSE, because of the different structures of the $4f^{11}$- $4f^{14}$ complexes. For the latter complexes there is a further contribution to νLn-O arising from the effect of the reduced coordination. For this reason it is not permissible to interpolate between $4f^{7}$ and $4f^{14}$ configurations to determine the contribution of the ion size and mass (ν_0). Instead a linear extension of the $4f^{0}$ - $4f^{7}$ interpolation is employed since this approximates the shape of the interpolation line for the log β_3 plot (Fig. 9) where no structural complications are experienced. The difference, δ(νLn-O), between the observed frequencies and (ν_0) represents the contribution to νLn-O from the CF stabilization for the $4f^{0}$ - $4f^{10}$ complexes and the combined effect of the CFSE and reduced coordination number for the $4f^{11}$ - $4f^{14}$ complexes (see Table 22).

TABLE 22. Spectral and thermodynamic data for the LnT_3 complexes.

Complex	Electron Config.	$\log\beta_3$ [a]	$\delta(\log\beta_3)$	$-\Delta H_1$ [b] (kcal/mole)	ΔS_1 [b] (e.u.)	νLn-O (cm^{-1})	δ(νLn-O) (cm^{-1})
LaT_3	$4f^{0}$	15.31	0	2.48	20.0	479.5	0
CeT_3	$4f^{1}$	16.12	0.47	2.70	21.0	480.5	0
PrT_3	$4f^{2}$	16.39	0.39	2.82	20.7	482.5	1
NdT_3	$4f^{3}$	16.61	0.27	2.85	21.8	484	1.5
SmT_3	$4f^{5}$	17.19	0.16	2.81	22.2	487	2
EuT_3	$4f^{6}$	17.62	0.25	2.76	23.2	490	4
GdT_3	$4f^{7}$	17.72	0	2.72	23.1	487.5	0
TbT_3	$4f^{8}$	18.00	0	2.74	23.5	491	2.5
DyT_3	$4f^{9}$	18.40	0.11	2.80	23.7	492.5	3
HoT_3	$4f^{10}$	18.81	0.22	2.76	24.6	494.5	3.5
ErT_3	$4f^{11}$	19.15	0.27	2.79	25.2	504	12
TmT_3	$4f^{12}$	19.39	0.22	2.94	24.9	506.5	13
YbT_3	$4f^{13}$	19.83	0.26	3.12	25.5	509.5	15
LuT_3	$4f^{14}$	19.77	0	2.90	25.5	509	(13.5)

a. Ref. 74; b. Ref. 75.

Some further features of the vibrational spectra of the lanthanide tris tropolonates warrent discussion. Significant cation-ligand attractions in lanthanide complexes are often largely electrostatic in character. It has been suggested[79] that the bonding in lanthanide complexes resembles that of complexes of the alkali earth ions rather than those derived from 3*d* transition metal ions. However the relatively high values of log β_3 and the high solubility of the monomeric complexes in organic solvents are indicative of considerable covalency in the lanthanide-oxygen bonds.

Furtheremore, reduced covalency in metal-β-ketoenolates[80] generally leads to a reduction in νM-O and an increase in νC-O, but these frequencies in the lanthanide tropolonates spectra are comparable with the values observed in the spectra of the 3*d* metal(III) tropolonates. It is worth noting that the structurally different $4f^{11}$ - $4f^{14}$ complexes exhibit unique features in their spectra. In particular the absence of bands near 520, 770 and 930 cm^{-1} differentiates their spectra from those of the polymeric lanthanide tropolonates.

(iii) Structural Features of the Lanthanide Tropolonates.

Having discussed the vibrational spectra of the various lanthanide tropolonates, it is of interest to note one or two features related to their structures. Muetterties and Wright[9] classified the lanthanide tropolonates into three structurally distinct series: (a) the monomeric $[LnT_4]^-$ species with 8 coordination; (b) the polymeric $[LnT_3]_n$ series with Ln = La through to Ho; and (c) the $[LnT_3]$ series with Ln = Er through to Lu.

There are significant differences between the vibrational spectra of members of groups (b) and (c) to account for a higher coordination number in the former than occurs in the latter. These assumptions would account for the solubility of the group (c) complexes relative to those of group (b). The group (a) complexes have 8 coordination and are monomeric. A crystal structure has been reported for the ammonium salt of $[HoT_4]^-$ [12] which was found to be 8 coordinate and to have a distorted trigonal dodecahedral configuration. It is possibly the crystal packing, influencing the amount of distortion, which accounts for the differences in the vibrational spectra of $Li[LnT_4]$ and $Na[LnT_4]$ complexes.

Six coordination is rare in lanthanide compounds, the complex usually manages to bind anions (or cations) or becomes hydrated, to increase its coordination number. Attempts to dehydrate lanthanide acetylacetonates[81] usually lead to extensive degradation. Therefore, although the group (c) compounds suggest low coordination number, there is some doubt as to this group being 6-coordinate. Although the solubility of the group (c) compounds suggests possible monomeric structures, tris(2,2,6,6-tetramethyl-3,5-heptanedionato) praseodynium(III) has been found crystallographically[82] to be a dimeric, 7 coordinate species and is soluble in most organic solvents[83]. The dimeric structure is achieved by the sharing of oxygen atoms between two Pr atoms, leading to trivalent oxygen atoms in the molecule.

Further there are sufficient similarities in the vibrational spectra of members of group (a) and (c) to suggest that 8 coordination may be common to both groups, the

relatively minor differences between the spectra being attributed to the fact that the (a) group complexes are monomeric while the (c) group complexes must necessarily be polymeric in order to achieve 8 coordination. If the complexes of groups (a) and (c) are both 8 coordinate, then the significant increase in νLn-O accompanying the structural transition preceding [ErT_3] would imply that the tropolonate complexes of the larger lanthanide ions have a coordination number exceeding eight. In the absence of crystallographic data these alternative structures must remain unresolved.

(iv) Ethylenediamine Complexes of the Lanthanide(III) Ions.

The lanthanide tropolonates are among the few series of lanthanide complexes which have been reported in an anhydrous form. The lanthanide ions prefer coordination numbers greater than 6 and sometimes as high as 9 and 10. It is interesting to compare other systems with the tropolonate results to see the effect that coordination number has on the lanthanide ion, especially in the solid state.

Forsberg and Moeller[84,85] have prepared, under anhydrous conditions to eliminate competition by water, a series of tris and tetrakis ethylenediamine complexes of the lanthanide(III) ions, with nitrate, perchlorate, chloride and bromide as anions. The tetrakis complexes with nitrate are of interest as the vibrational spectral studies indicate a structural change from $[Ln(en)_4(NO_3)](NO_3)_2$ (for Ln = La through to Sm), to $[Ln(en)_4](NO_3)_3$ (for Ln = Eu through to Yb). Thus a change in coordination number from 9 to 8 occurs at Eu and with the larger lanthanide ions, the nitrate ion is bound directly to the metal ion to satisfy the bonding

3. VIBRATIONAL SPECTRA OF THE NON-TRANSITION METAL TROPOLONATES.

Relatively little work has been done on the vibrational spectra of non-transition metal complexes and none on the complexes of tropolone. Some work has been done on the β-ketoenolate complexes. As all CF effects are absent from the non-transition metal complexes, some other basis for the interpretation of the trends shown by νM-O must be found. At the same time some insight might be obtained as to the factors, other than CF effects, which do influence νM-O and which are described by $-E_r$ in the thermodynamic treatment of CFT[2] . $-E_r$ increases with increasing atomic number and is ascribed to the ionic contraction of the metal ions. A study of non-transition metal complexes affords an opportunity of determining factors, besides CFSE, which influence the strength of metal-ligand bonding, and thus νM-O. Among the factors which might contribute to the metal-ligand bonding are mass of central metal ion, the ionic change of the metal ion and the ionic radius and ionization potential with which is associated the ability to attract electrons to the metal ion.

The non-transition metal tropolonate vibrational spectra have various band patterns below 700 cm^{-1}, governed by the type of bonding and structure present in the complex, so that it is not possible to assign and compare all the metal sensitive bands of all the non-transition metal tropolonates. In order to overcome this problem, only the two most metal sensitive bands have been assigned and used in this study (see Fig. 15). It is possible in some

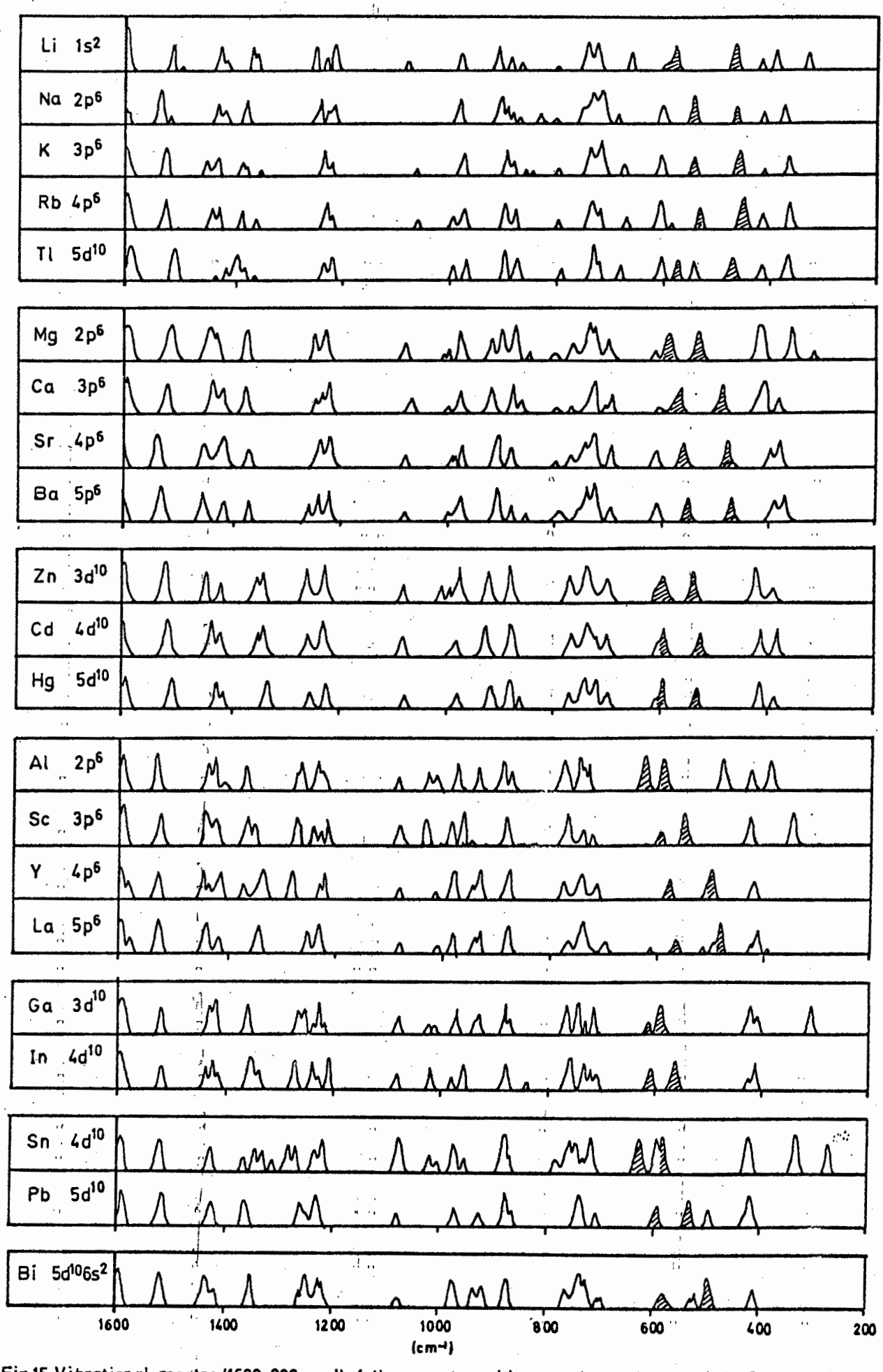


Fig.15. Vibrational spectra (1600-200 cm^{-1}) of the non-transition metal tropolonates ($\nu M-O_1$ and $\nu M-O_2$ are shaded).

instances to assign these two bands by comparing the spectra of unassigned compounds, with that of some compound in the same group which has been assigned from either the study of the transition metal tropolonates or the lanthanide tropolonates (i.e. the alkali metal tropolonate spectra can be assigned from the spectra of CaT_3; the bands from the spectra of AlT_3 and InT_3 from that of GaT_3; the bands from the spectra of CdT_2 and HgT_2 from that of ZnT_2). In all cases the two most metal sensitive bands (described here as $\nu M\text{-}O_1$ and $\nu M\text{-}O_2$) are based on the two bands which shift most on isotopic labelling of CuT_2[21] and the corresponding bands which shift most on substitution of metal ions for the di- and trivalent transition metal tropolonates and the lanthanide tropolonates. The compounds where there are no comparisons within the group, namely the compounds of alkali and group IV, have $\nu M\text{-}O_1$ and $\nu M\text{-}O_2$ assigned by comparison with the spectra of similar compounds from other groups.

It is interesting to note that there is not the disparity expected between $\nu M\text{-}O_1$ and $\nu M\text{-}O_2$ for the spectra of ionic and covalent complexes (e.g. alkali metal complexes and group III complexes). The values of $\nu M\text{-}O_1$ and $\nu M\text{-}O_2$ for the alkali and alkali earth tropolonates seem rather high in view of their supposed ionic character. A similar effect is noted for the vibrational spectra of alkali metal acetylacetonates[86-87]. This implies that, at least in the solid state, these complexes might have some covalent character. This is supported by the findings of a crystallographic study of NaT[88] which shows that the Na-O bond distances vary from 2.37 to 2.60 Å which is shorter than might be expected for a purely ionic bond.

(i) The Effect of Mass of the Metal Ion on the Metal Sensitive Frequencies.

In general, for simple diatomic molecules, the stretching frequency of the bond, $\nu(cm^{-1})$ is inversely proportional to the square root of the reduced mass of the molecule. That is, as the reduced mass of the molecule increases, the stretching frequency decreases. Thus not only the bond strength (associated with the force constant), but also the reduced mass of the molecule influence the stretching frequency. If this argument is extended to include polyatomic molecules, then at least on a qualitative basis, increased mass of the metal ion in a complex should lead to a decrease in νM-L for the complex.

In Table 24 pairs of metals are compared, which have similar ionic charge and ionic radius, but which differ in the mass of the metal ion. It would thus be expected that νM-O would show a decrease as the mass of the metal ion increases. In no case is this observed as νM-O invariably shows some increase with increasing mass, although this is sometimes small. Thus it could be assumed from these observations that νM-O is roughly independent of the mass of the metal ion.

This finding is in agreement with the transition metal complexes of tropolone where $-E_r$ increases with increasing atomic number (based on the interpolation between d^0, d^5 and d^{10} where CFSE is zero). As the influence of the mass of the metal ion would be expected to cause a decrease of $-E_r$, obviously the influence of the mass is small (or non-existent) and is negligible compared to the other factors causing $-E_r$ to increase.

TABLE 24. Comparison of νM-O for tropolonate complexes with non-transition metal ions of similar ionic charge and radius but differing mass.

Ion	Ionic Radius r^+ (Å)	Mass of Ion (a.m.u.)	$\nu M-O_1$ (cm^{-1})	$\nu M-O_2$ (cm^{-1})
Sc^{+++}	0.81	44.956	544	583
In^{+++}	0.81	114.82	557	607
Mg^{++}	0.65	24.32	529	583
Zn^{++}	0.74	65.38	533	590
Ca^{++}	0.99	40.08	487	561
Cd^{++}	0.97	112.40	522	587
Sr^{++}	1.13	87.62	475	553
Hg^{++}	1.10	200.59	526	590
Rb^{+}	1.48	85.47	455	536
Tl^{+}	1.44	204.37	472	574

In similar work on the non-transition metal acetylacetonates, Hancock[71] also noted that νM-O was independent of the mass of the metal ion, for metal ions of similar ionic charge and ionic radius. He further showed that if the effect of the other metal-oxygen bonds in the molecule are taken into account, then the change of mass does not have such a marked influence on the stretching frequency of the bond. However for this calculation a simplified model was used based on an octahedral complex with the oxygen atoms not vibrating with the metal ion alone (diatomic model), but with the metal ion plus five other oxygen atoms. The calculations can therefore give no more than a qualitative indication of the effect of changing mass.

It therefore seems probable that the effects of increase of mass, even where these are large, have little or no influence on νM-O and this factor might be neglected in a consideration of non-transition metal stretching frequencies.

(ii) The Influence of Ionic Charge (Valence) of the Metal Ion on the Metal Sensitive Frequencies

The ionic charge of the metal ion has two distinct effects on the strength of metal-ligand bonding. Increased positive charge on the metal ion enhances the attraction for negatively charged ligands, thus increasing the M-O bond strength. As the ionic charge increases, the valence of the metal ion increases and the bonding power of the metal ion must be spread over more metal-ligand bonds, leading to a weakening of the M-O bonds. This increase in coordination number implies structural changes which could also have some effect on bond strength.

Proceeding across a period of elements, the ionic charge of the metal ion increases by one for each successive element to a formal charge of three (or in some instances four). While the ionic charge increases, the mass change is relatively small but the ionic radius of the metal ion decreases. A plot of νM-O against ionic charge of metal ion (Fig. 16) shows an increase in νM-O as ionic charge is increased. The elements of the various periods are grouped into sets with empty outer *d* orbitals (the A groups of elements of the periodic table i.e. K, Ca and Sc) and sets with filled outer *d* orbitals (the B groups of elements

of the periodic tables i.e. Cd, In and Sn). Thus Al is grouped with Sc, Y and La and not Ga and In as it has a closer resemblance to the A group elements (with vacant *d* orbitals) than to the B group elements (with filled *d* orbitals). It can be seen from Fig. 16 that νM-O for compounds of the B group elements are generally higher than νM-O for those of the A group elements of the corresponding period. The filled *d* orbitals have a stabilizing effect, which might be due to the decrease in ionic radii which occurs on filling the *d* orbitals. It could also be due to some back donation of *d* electrons to the ligand resulting in π bonding which could serve to increase νM-O.

The increase in νM-O observed in Fig. 16 might not be due only to ionic charge, but also to the decrease in ionic radius which occurs concurrently with change in ionic charge within the period. It is preferable to choose elements from different periods, which have similar ionic radii. When this is done, the metal ions chosen have greatly differing masses. However it has already been established in the previous section that the effect of mass on νM-O is negligible. Fig. 17 depicts plots of νM-O against ionic charge of metal ions with similar ionic radii. It is observed that νM-O still increases with increasing ionic charge, but the observed increase is smaller than that observed in Fig. 16 where the ionic radius also varied. This implies that the attracting force of the increased nuclear charge of the metal ion has a stronger influence on the M-O bond strength, than does the increased number of M-O bonds associated with the higher valence of the metal ions.

The effect of increased number of M-O bonds does

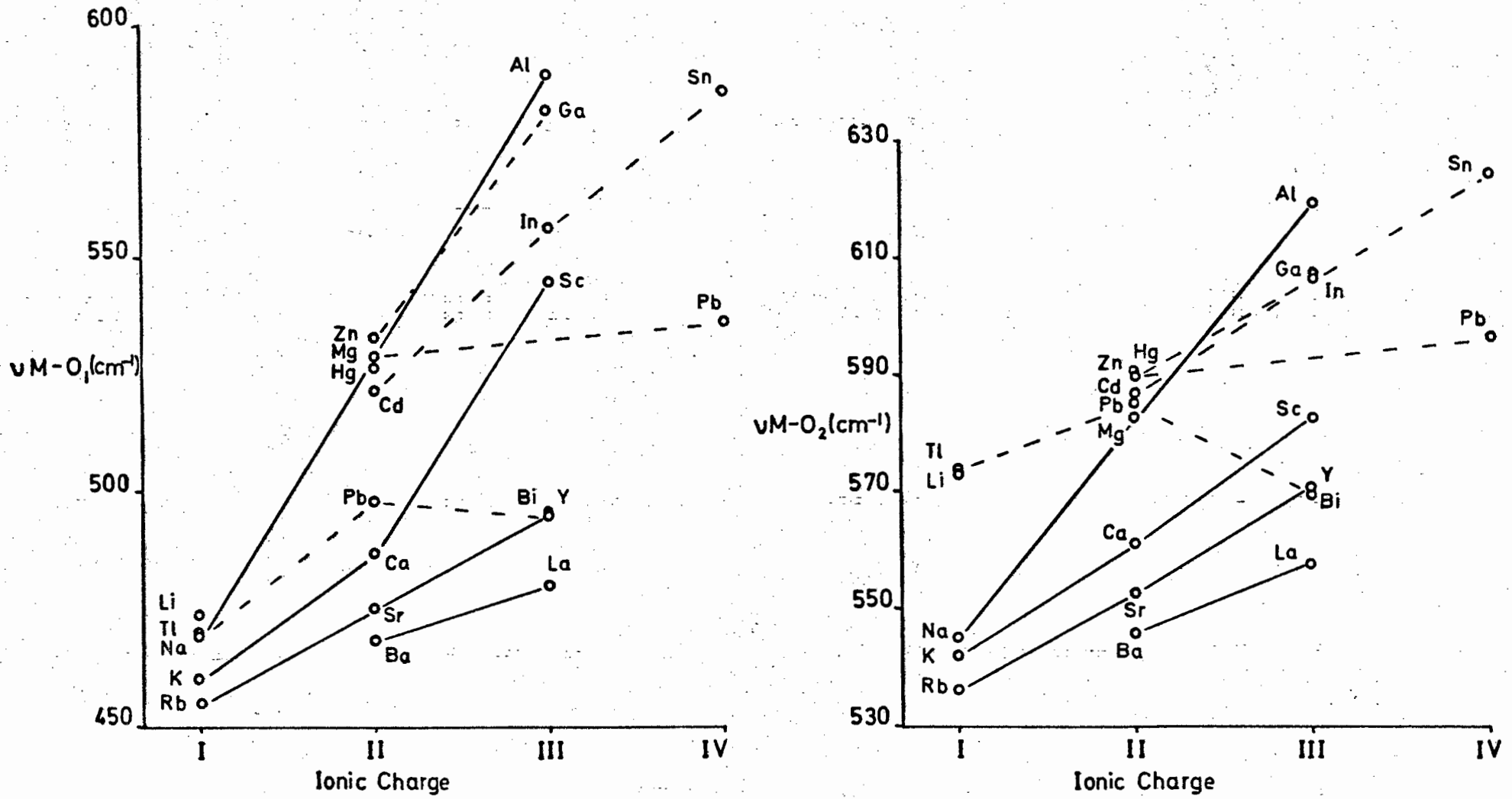
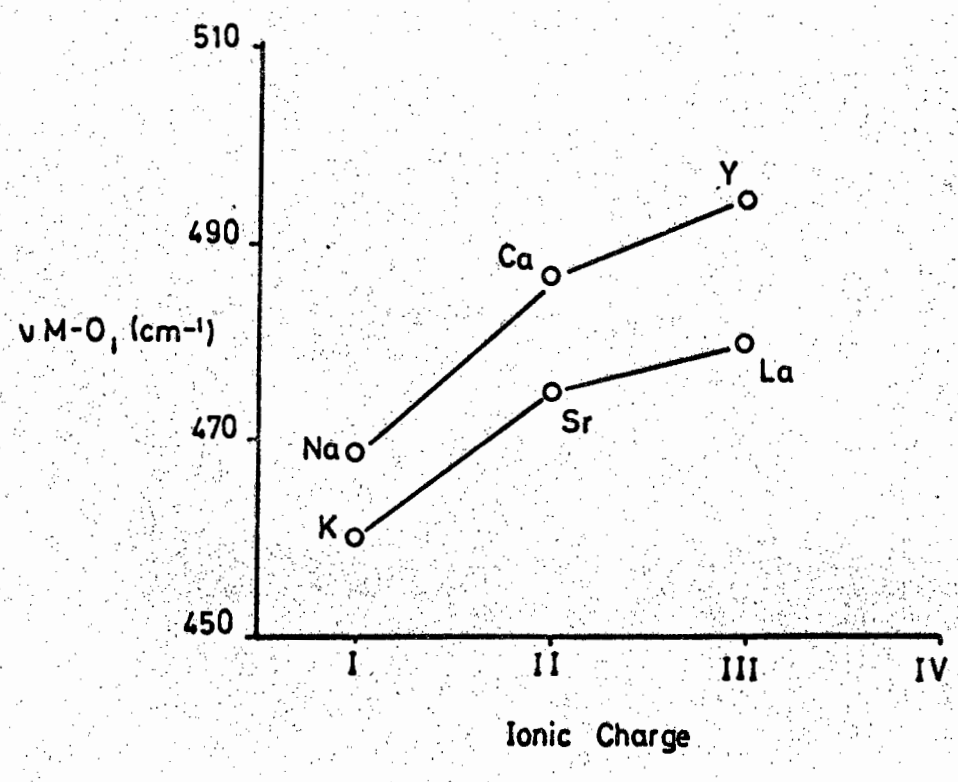


Fig.16. Effect of increasing ionic charge on νM-O across non-transition metal periods.



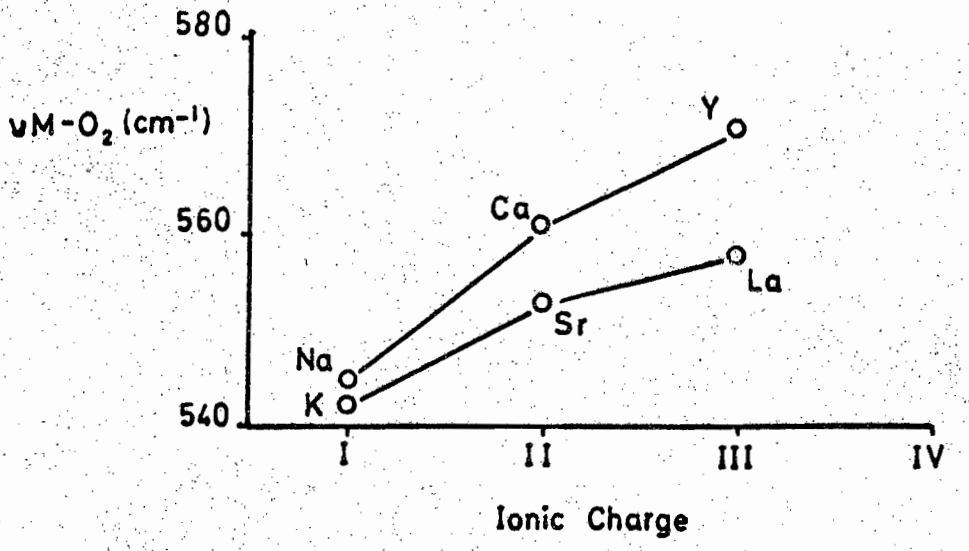


Fig.17. Effect of increasing ionic charge on νM-O for complexes of similar ionic radius.

contribute to the weakening of the M-O bond strength. This can be seen for the compounds $[BiT_2]Cl$ and BiT_3, where Bi has an ionic charge of +3 for both compounds. $[BiT_2]Cl$ has four M-O bonds and $\nu M\text{-}O_1$ is 513 cm^{-1}, while BiT_3 has six M-O bonds and $\nu M\text{-}O_1$ is 495 cm^{-1}.

In all these comparisons of complexes where the metal ions differ in valence, it must be remembered that associated with the change in valence is a possible change in bonding and structure of the complexes, which could also influence the observed trends. The alkali metals are sometimes hydrated and little is known of their structures. A crystal structure of NaT[88] shows that the Na ion has six oxygen neighbours with Na-O distances from 2.37 to 2.60 Å. The compound is found to be anhydrous. The alkali earth complexes are anhydrous and it is possible that they have either tetrahedral or polymeric octahedral structures[11]. The trivalent group IIIA and B compounds are anhydrous and GaT_3 has been shown to be monomeric[7]. These compounds all have octahedral structures. ZnT_2 is probably polymeric octahedral, but CdT_2 and HgT_2 are likely to have tetrahedral structure. These different structures probably have some effect on the bond strength and thus $\nu M\text{-}O$ and it is impossible to exclude their influence on the overall trends observed for ionic charge.

(iii) The Influence of Ionic Radius (r^+) and Ionization Potential (I_Z) on the Metal Sensitive Frequencies.

A study of the values of r^+ and I_Z reveal trends within the periodic table of the elements. Within a group

I_z decreases and r^+ increases with increasing atomic number. Within a period I_z increases and r^+ decreases with increasing atomic number. From these trends it is assumed that some relationship must exist between I_z and r^+. The ionization potential is a measure of the force of attraction between the nucleus and the outer electrons of an atom or ion. It is a property that can readily be measured by physical means, with some degree of accuracy. The ionic radius of an ion is dependent on the contraction of the outer electrons due to the attractive force of the nucleus for the remaining electrons. The ionic radius is calculated from the measured bond lengths of various molecules. Both have a dependence on the attractive force of the nucleus and should therefore have come interrelationship.

In practice the relationship is not as simple as is at first implied because many factors influence these two properties. A primary influence is the fact that the outer shell does not always have a maximum capacity of 8 electrons, but sometimes less ($Li^+ \rightarrow F^{7+}$) and sometimes more (due to the introduction of *d* and *f* electrons). Both these factors influence the nuclear attraction. A relationship,

$$I_z \propto \frac{1}{\sqrt{r^+}} \qquad (11)$$

has been found for the groups $Na^+ - K^+ - Rb^+ - Cs^+$ and $Mg^{2+} - Ca^{2+} - Sr^{2+} - Ba^{2+}$[89,90], but this excludes Li^+ and Be^{2+} as they are not 8 electron systems, nor can the relationship be extended, in view of the influence of *d* and *f* orbitals in other groups.

The covalency of a bond depends on the polarizing power of an atom or an ion. This may be expressed as the ability of a cation to attract electrons from an anion so that they are held together by a covalent bond (sharing of electrons), rather than by ionic forces of attraction. This polarizability is dependent on the attracting power of the nucleus. Further, the smaller the cation, the greater the charge density and the greater the polarizability. Therefore both I_z and r^+ are indirect measures of polarizability.

For metal complexes, the metal-ligand bond strength will be determined by the ability of the metal cation to attract ligand electrons to itself, forming coordinate bonds. Thus the bond strength will be determined by the amount by which the metal-ligand bond is polarized, that is the bond strength increases with increasing covalency of the metal-ligand coordinate bond. Thus it should be possible to relate parameters of bond strength - such as the metal sensitive stretching frequencies of vibrational spectra - to the polarizability (as represented by either I_z or r^+). The bond strength should increase with increase of I_z, due to the greater attraction of the nucleus, and increase with decrease of r^+, as the charge density will be inversely proportional to r^+.

The metal sensitive frequencies are observed to follow qualitatively the changes of I_z and r^+. As I_z decreases in proceeding down a group, so νM-O decreases. Similarly, as I_z increases in proceeding across a period the charge density increases rapidly due to the increase in the formal ionic charge and the decrease in r^+, giving rise to an increase in νM-O. The trends can be seen in

Table 25 and in Fig. 18 which shows a plot of νM-O against I_z (where I_z is the first ionization potential for monovalent ions, the second ionization potential for divalent ions, etc.).

TABLE 25. Ionization potentials, ionic radii and metal sensitive frequencies for non-transition metal tropolonates.

Ion	νM-O_1 (cm^{-1})	νM-O_2 (cm^{-1})	I_z (e.V.)	r^+ (Å)	$\frac{1}{r^+}$ ($Å^{-1}$)	$\frac{1}{\sqrt{r^+}}$ ($Å^{-\frac{1}{2}}$)
Li^+	473	573	5.39	0.68	1.47	1.21
Na^+	469	545	5.12	0.97	1.03	1.02
K^+	460	542	4.34	1.33	0.75	0.87
Rb^+	455	536	4.18	1.47	0.68	0.82
Tl^+	472	574	6.11	1.44	0.69	0.83
Mg^{++}	529	583	15.03	0.66	1.52	1.23
Ca^{++}	487	561	11.87	0.99	1.01	1.01
Sr^{++}	475	553	11.03	1.12	0.89	0.95
Ba^{++}	468	546	10.0	1.34	0.75	0.86
Zn^{++}	533	590	18.0	0.74	1.35	1.16
Cd^{++}	522	587	16.9	0.97	1.03	1.02
Hg^{++}	526	590	18.8	1.10	0.91	0.95
Al^{+++}	590	620	28.4	0.51	1.96	1.40
Sc^{+++}	544	583	24.8	0.81	1.24	1.11
Y^{+++}	495	571	20.5	0.92	1.09	1.04
La^{+++}	480	558	19.2	1.14	0.88	0.94
Ga^{+++}	582	607	30.7	0.62	1.61	1.27
In^{+++}	557	607	28.0	0.81	1.24	1.11
Bi^{+++}	495	570	25.56	0.74	1.35	1.16
Sn^{++++}	586	625	40.72	0.71	1.41	1.19
Pb^{++++}	537	597	42.31	0.84	1.19	1.09
Pb^{++}	498	585	15.04			

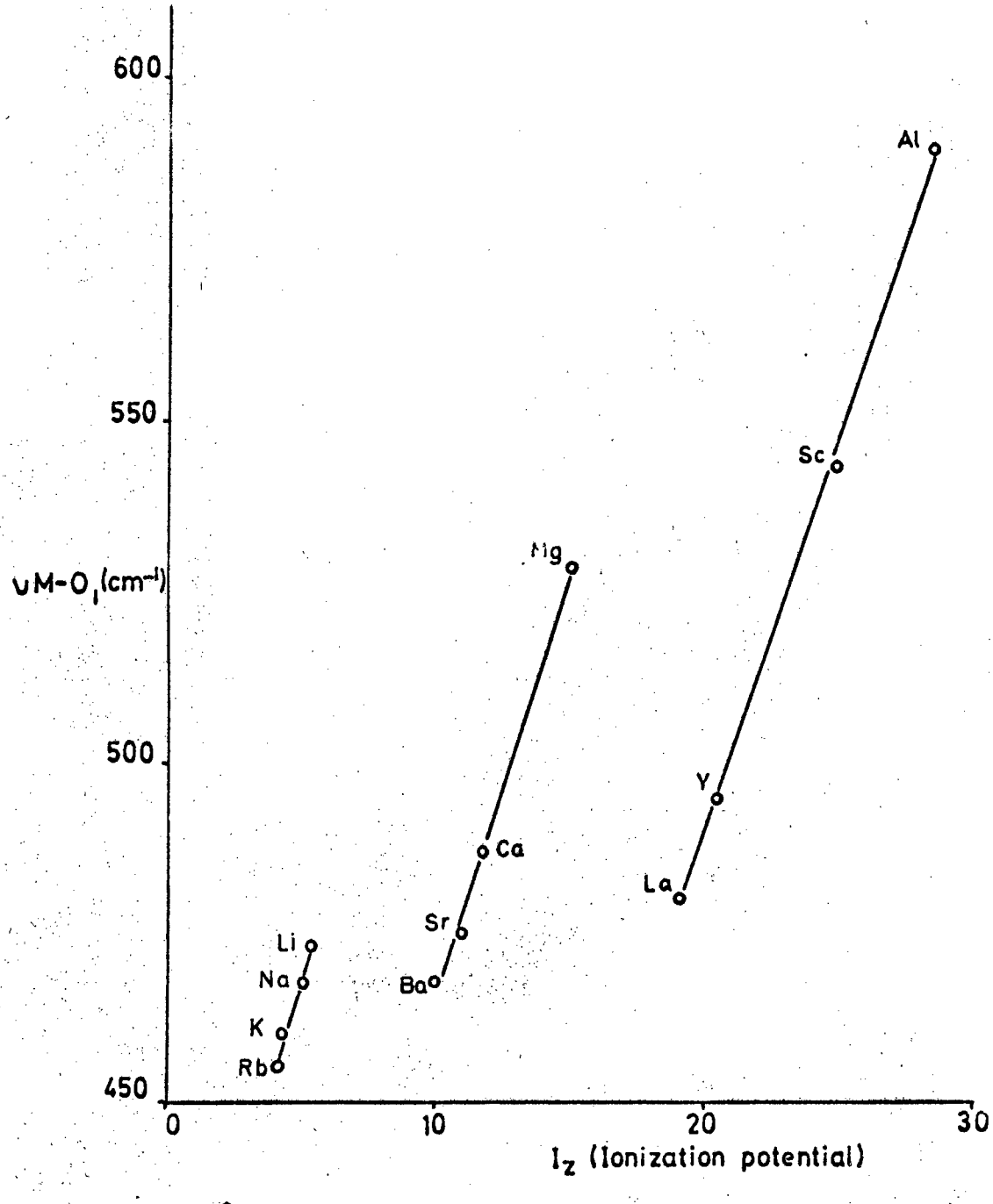


Fig.18a. Plot of $\nu M\text{-}O_1$ against ionization potential for non-transion metal tropolonates.

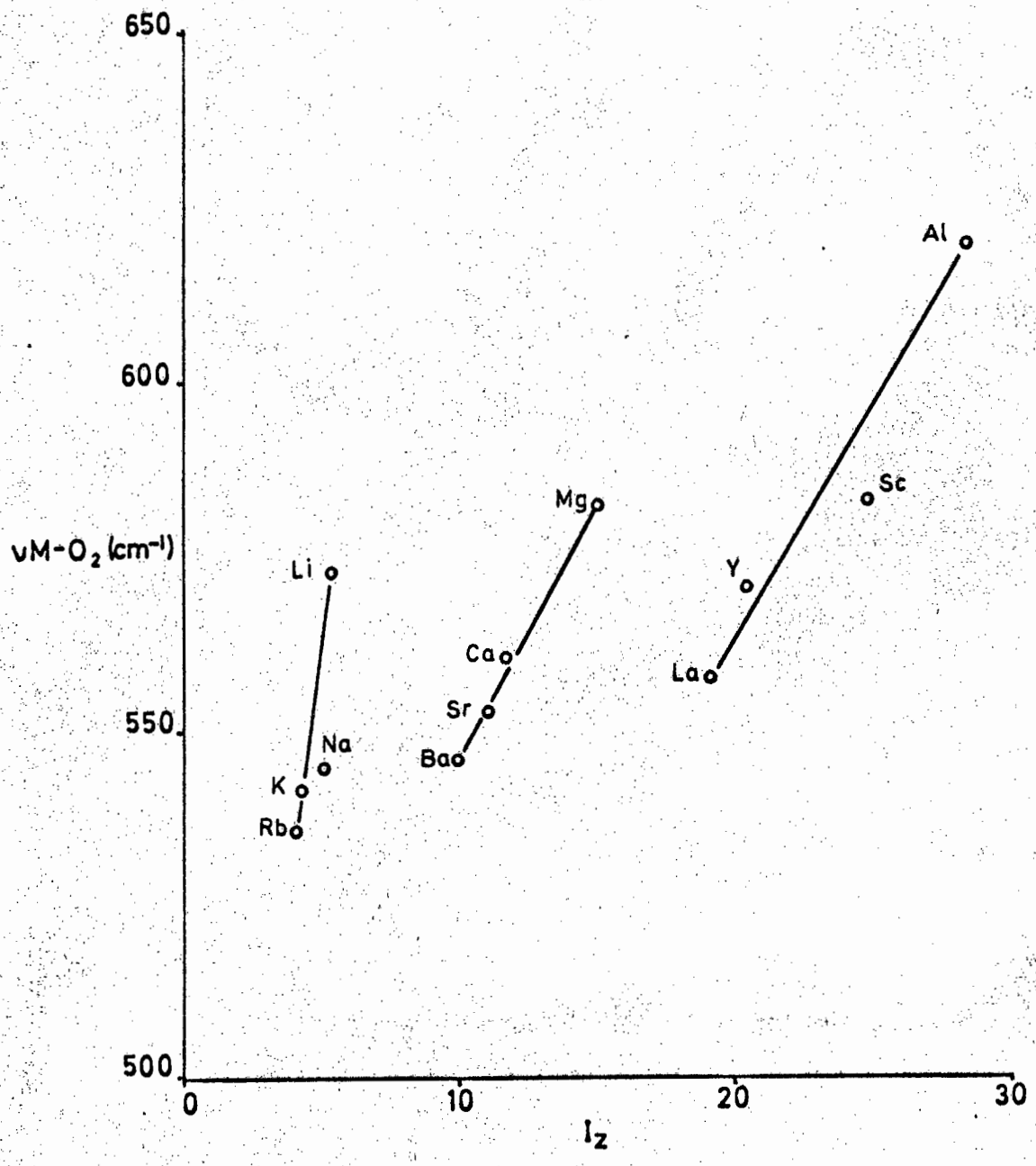
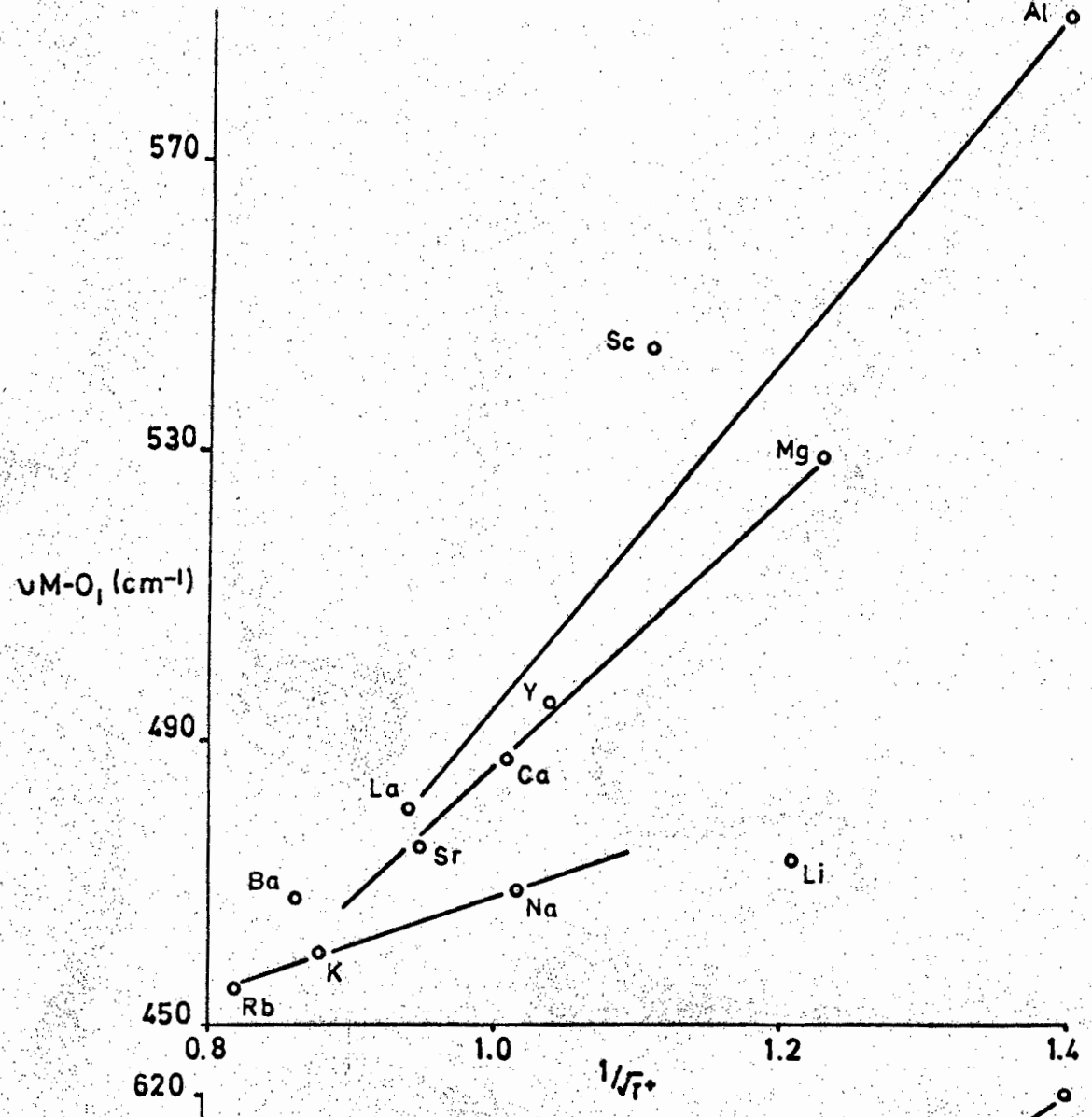


Fig.18 b. Plot of $\nu M\text{-}O_2$ against ionization potential for non-transition metal tropolonates.



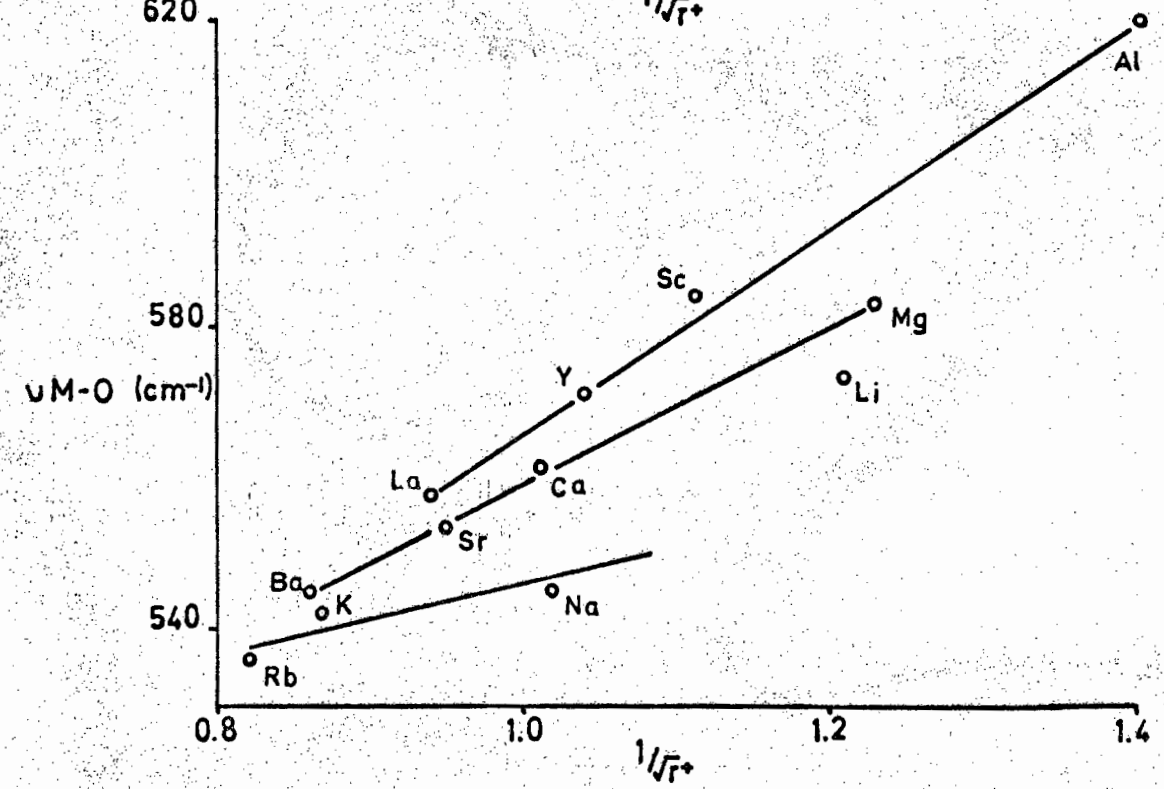
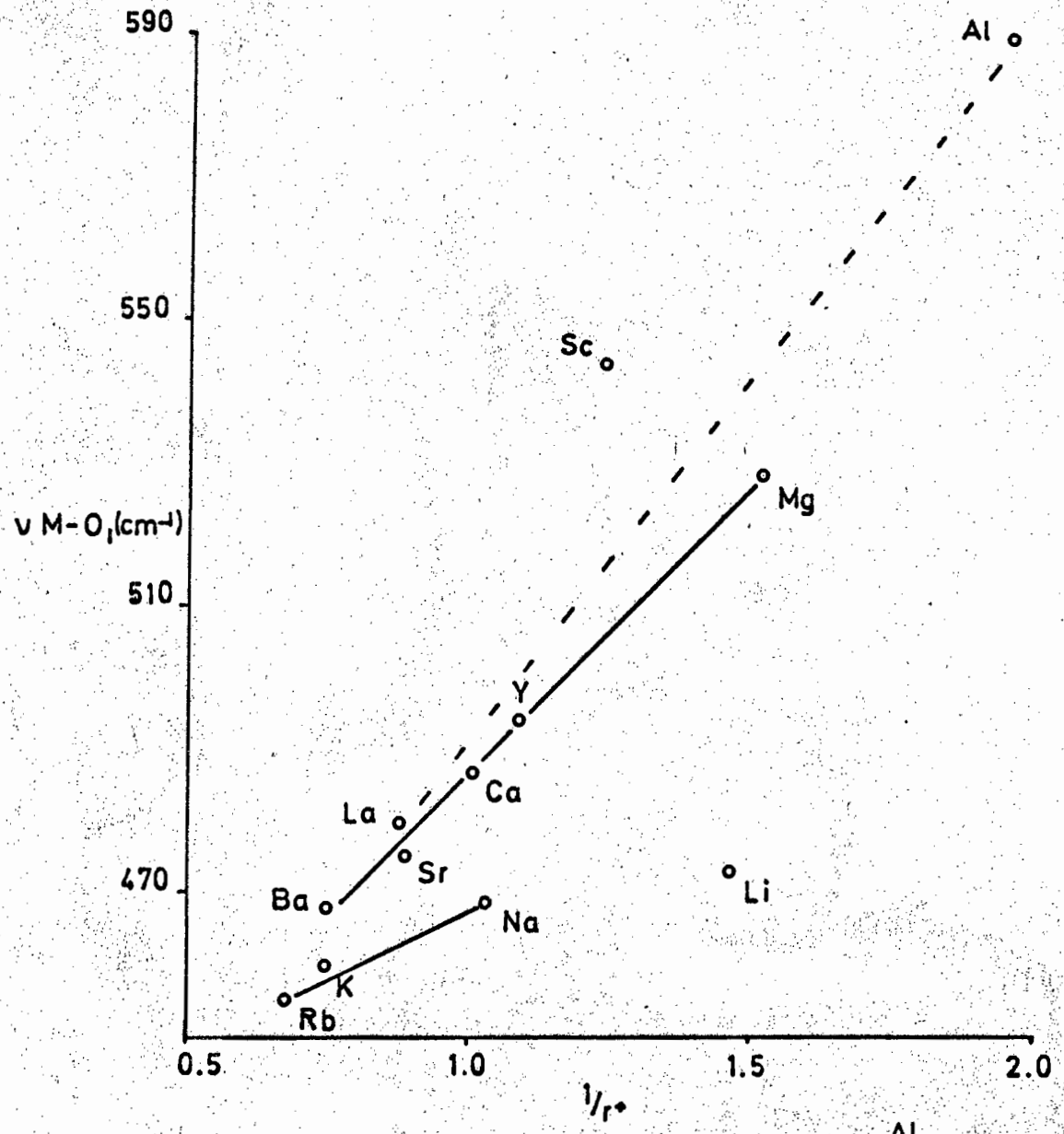


Fig.19. Plot of νM-O against $1/\sqrt{r}$+



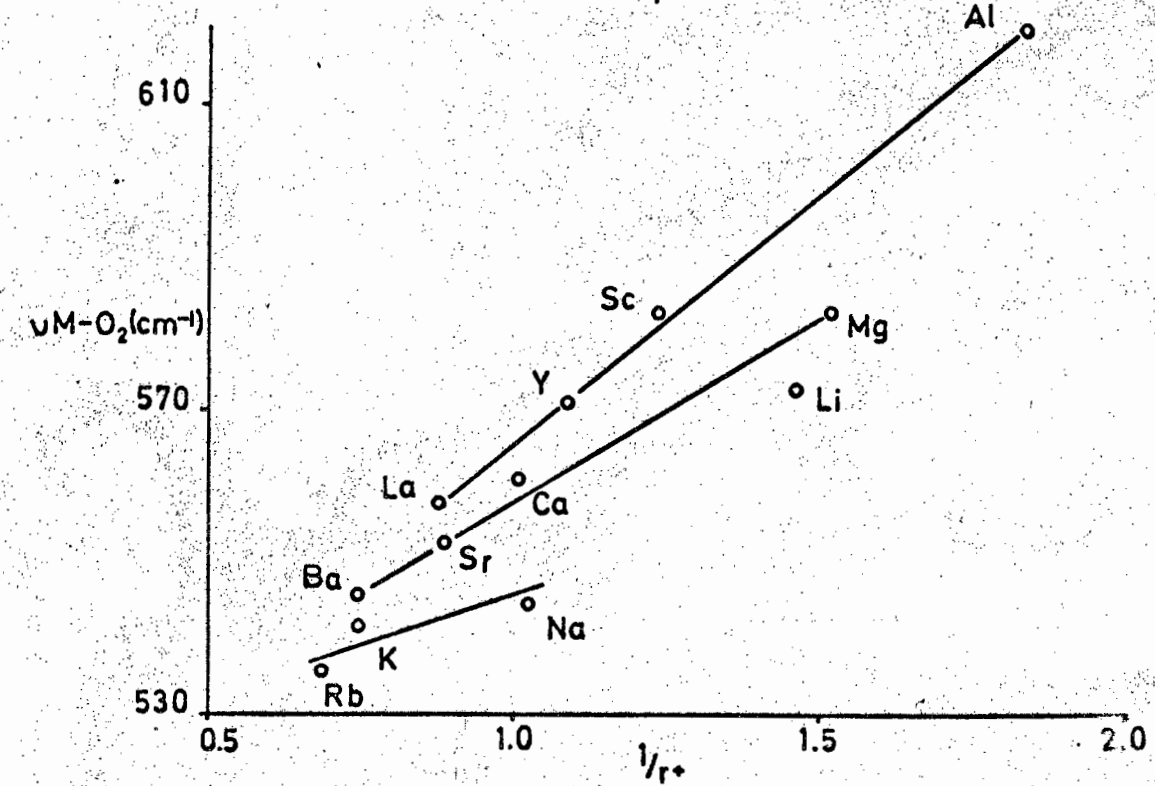


Fig.20. Plot of νM-O against $^{1}/_{r^{+}}$ (the inverse of ionic radius)

On this qualitative basis it can be seen that there is not only an agreement between I_z and νM-O, but also that there is agreement between νM-O and increased covelancy (polarizability). It is well known[91] that compounds of successive elements in a period become more covalent (Na forms ionic compounds while Al forms covalent compounds). Also in proceeding down a group the compounds become more ionic (Li and Be form reasonably covalent bonds, while the heavier elements of these groups tend to have ionic characteristics). This is reflected in the changes in νM-O which is seen to be high for covalent complexes but low for more ionic complexes.

Fig. 18 shows that linear relationships between I_z and νM-O exist for the alkali, alkali earth and group IIIA metal tropolonates. It is however surprising that LiT occurs on the straight line through the alkali tropolonates, as Li^+ is not an 8 electron ion and might be expected to differ from the other alkali tropolonates. Linearity is observed not only within groups, but also there is an approximate linear relationship for the complexes within each period involving much larger changes in I_z.

Linearity is observed for plots of νM-O against $1/\sqrt{r^+}$ (Fig. 19) which is expected from equation (9)[89,90]. For this plot it is seen that LiT deviates from the straight line drawn through the other alkali tropolonates, which is in accordance with the previous work on this relationship[89,90]. It is of interest to plot νM-O against $1/r^+$ (Fig. 20). The inverse of r^+ must be proportional to the charge density, as a decrease in r^+ causes an increase in charge density. The

plots show a linear (or near linear) trend for the alkali, alkali earth and group III metals, indicating that νM-O has a dependence on charge density. As both charge density and I_Z can be related to the polarizability of the cation it is concluded that the strength of metal-ligand bonding (as reflected by νM-O) is governed by the polarizability of the bond.

It can be concluded that for non-transition metal complexes, the mass of the cation has little effect on νM-O, but the dominating factor is the polarizability. This polarizability is the attraction of the nucleus of the metal cation for electrons from the ligand anions and can be related to I_Z and r^+ (and ionic charge which also influences the charge density) which are measures of this attraction.

4. THE ULTRAVIOLET/VISIBLE (UV) SPECTRA OF THE METAL TROPOLONATES.

The uv spectra of the first transition series trivalent metal tropolonates have been determined by transmission through solutions of $CHCl_3$ and CH_3OH and by reflectance of solids on filter paper (see Table 19). There are three bands in the uv region of all the metal complexes. These occur at about 26000 cm^{-1}, 30000 cm^{-1} and 40000 cm^{-1} and are labelled bands 1, 2 and 3 respectively. They correspond to the three bands observed for tropolone itself[92], which occur at 26300-29400 cm^{-1}, 31250 cm^{-1} and 43500 cm^{-1}. These three bands are assigned to various $\pi \rightarrow \pi^*$ transitions of the tropolone molecule.

The assignment of these bands is based on a study of polarized spectra of tropone and tropolone[92] and

SCF MO calculations on tropone and tropolone[93]. Band 1 is associated with the 33000 cm^{-1} band of tropone and is assigned to local excitation in the ring. This band is shifted to lower energy in tropolone, probably due to the influence of the hydroxyl group on the energy of the ring π orbitals. Band 2 at 31250 cm^{-1} has been assigned, on the basis of the polarization effect parallel to the C-OH bond, as a charge transfer band from the hydroxyl group to the seven-membered ring. However the molecular orbital calculations show that the orbital associated with the hydroxyl group is not involved in this transition and consequently doubt is placed on this assignment. Band 3 at 43500 cm^{-1} is associated with the electron transfer from the π orbitals of the seven-membered ring to the π^* orbital of the carbonyl.

There are no bands found in the trivalent metal tropolonates which correspond with the $d \rightarrow \pi^*$ transitions, sometimes found in other metal complexes. This does not imply that such transitions do not take place. However as they occur in the same region (25000 - 30000 cm^{-1}) as bands 1 and 2, which are intense, as the selection rules allow $\pi \rightarrow \pi^*$ transitions, they are probably masked by these bands.

The assignment of the other bands is based mainly on the previous work on metal complexes and metal acetylacetonates in particular. This is justified as the other bands, which occur in the visible region are due to transitions involving orbitals of the metal and are not directly dependent on the ligand orbitals. The assignments (where possible) are shown in Table 19.

The $\pi \rightarrow \pi^*$ transitions afford an opportunity for

determining the extent of metal-ligand π interaction within the complexes. Any interaction between metal *d* orbitals and ligand π and π* orbitals shift them further apart energetically[94]. Thus the greater the energy of the π → π* transition, the larger the amount of metal-ligand π interaction. This is indicated by the uv spectra of the trivalent metal acetylacetonates where an order of π bonding strength is derived from the π → π* transition. The order observed is Co>Cr~Fe>Mn~V[95]. It can be seen that this order does not conform to a simple dependence on *d* orbital population. Rather the total π interaction tends to increase with *d* orbital population except that it is particularly large for Cr(III) and small for Mn(III). It was further found[96] from a combination of uv and nuclear magnetic resonance spectroscopic results, that the donor M → π* bonding is weak and diminishes with increasing atomic number except for low spin Co(III) which has substantial donor bonding. Acceptor π → M bonding tends to be a more dominating effect and increases with increasing atomic number (but absent for Co(III)).

As no nuclear magnetic resonance study exists for the trivalent metal tropolonates, it is assumed that the π bonding order is similar to the trivalent metal acetylacetonates. Further, there are three separate π → π* transitions which involve various π orbitals of the tropolonates ion and which might be affected differently, according to the nature of the metal-ligand π interaction. The observed bands vary and are in the following order of decreasing transition energy

Band 1. V~Fe>Mn>Cr~Co

Band 2. V>Fe>Cr>Mn>Co

Band 3. V>Fe~Cr>Co>Mn.

It can be seen that V(III) and Fe(III) have stronger interaction with the tropolonate π bonds, than the other metal ions. V(III) is the ion with the strongest donor π bonding capacity and Fe(III) the ion with the strongest acceptor capacity, in the case of the acetylacetonates[95]. This excludes Co(III) which has strong donor π bonding capacity, but is seen to have relatively weak interaction. Possibly this is a consequence of its low spin configuration. The position of Mn(III) is seen to vary relative to the other ions. Mn(III) acetylacetonate is found to be relatively ionic[3] compared to the other trivalent acetylacetonates and this might also be the case for MnT_3. If this is so, then it is possible that this ionicity has some varying influence on the three $\pi \rightarrow \pi^*$ bands.

However, in the absence of a molecular orbital calculation for trivalent metal tropolonates, the difficulty of assigning bands, or predicting the π interactions precludes a more detailed explanation of the π bonding.

It has been mentioned previously that tropolone can be assumed to have a similar position to that of acetylacetone on the spectrochemical series and thus a similar value of δ (namely 1.2). It is possible to obtain a measure of the value of δ for tropolone by observing the $^4A_2g \rightarrow {}^4T_2g$ transition in Cr(III) complexes[97]. This transition is a direct measure of 10 Dq. The value of g for the Cr(III) ion calculated from this method is 17.0 kK using the hexahydrate ion. This method gives an δ value for the acetylacetonate ion of 1.05. The value calculated for the tropolonate ion is 1.06 using the 17980 cm^{-1} band for CrT_3. This is close to the value for acetylacetone

and therefore justifies the use of similar δ values for tropolone and acetylacetone, namely 1.2, as given by Figgis[1] and generally in use.

5. THE METAL TROPOLONATE VIBRATIONAL SPECTRA.

(i) The Region 1600 - 1300 cm^{-1}

The metal tropolonate complexes have two bands at 1590 cm^{-1} and 1520 cm^{-1}. The β-ketoenolate metal complexes also have two bands in this region which are assigned to $\nu C=C$ and $\nu C=O$ and analogous assignments for the corresponding two bands in the tropolonates has generally been assumed. The band at 1590 cm^{-1} has been assigned to $\nu C=O$ by previous workers[37]. However this band does not appear to be particularly sensitive to metal ion substitution. The band at 1520 cm^{-1} shifts on changing the metal ion so that it is possible that this band represents $\nu C=O$. However Junge[21] has shown in his [^{18}O]-labelling study of CuT_2 that both these bands are insensitive to isotopic labelling and therefore have little $\nu C=O$ character. As the 1520 cm^{-1} band does show some metal sensitivity it is possible that there is some degree of coupling with a metal sensitive band, as the shifts are small and fairly random, the coupling must be comparatively small. Both these bands are therefore assigned to $\nu C=C$ vibrations of the tropolone ring. The bands in the 1400 - 1500 cm^{-1} range are likely to be either further $\nu C=C$ ring vibrations or else deformations of the C-H bonds ($\delta C-H$). Ikegami[17-19] assigns these bands to $\delta C-H$ on the basis of the differences observed for solid and solution spectra.

The band in the 1300 - 1360 cm^{-1} region is assigned by Junge[21] to νC-O, on the basis of [^{18}O]-labelling of CuT_2. This band is likely to be the most sensitive to metal ion substitution, after the νM-O bands. For the first transition series di- and trivalent metal complexes the observed order in which this band shifts is Ca>Mn~Co~Ni<Cu>Zn and Sc>Ti>V<Cr>Mn<Fe>Co<Ga. This order (for the trivalent complexes) is roughly the opposite of that observed for νM-O bands and predicted by CFSE. This implies that tropolonate complexes might maintain a constant bond order about the oxygen atoms, that is as the M-O bond is strengthened, so the C-O bond is weakened. The 1300 - 1360 cm^{-1} band in the LnT_3 complexes remains constant, but the same band for the $[LnT_4]^-$ ions increases steadily from 1357 cm^{-1} to 1370 cm^{-1}, with increasing atomic number. This is contrary to the observation for the transition metal complexes where the bond order of the oxygens was preserved, as the bond order of the oxygens now increases as the M-O bond is strengthened.

The relatively low 'carbonyl' frequency of the tropolonate complexes is noteworthy and is justified by the unusually high C-O bond distances of 1.32 and 1.28 Å, found in CuT_2. A similar situation is found for the bis(salicylaldiminato)- metal(II) complexes[50,98] which have νC-O at 1330 cm^{-1} and have C-O bond distances of 1.316 - 1.320 Å. The tropolonate ion in metal complexes, unlike the β-ketoenolates which have more carbonyl double bond character, has predominantly single bond C-O character. In the vibrational spectrum of tropolone[21] itself, both νC=O at 1547 cm^{-1} and νC-O at 1266 cm^{-1} and 1247 cm^{-1} are observed to shift on [^{18}O]-labelling. In the metal

complexes of tropolone, only νC-O is observed, but this has shifted by 50 - 100 cm^{-1} to higher frequency. From this it can be concluded that there is more bond delocalization in the metal complexes than in tropolone itself as the phenomenon of C=O and C-O bonds disappear and only one C-O vibration is observed somewhere between the two original vibrations of the tropolone molecule.

(ii) The Region 1300 - 700 cm^{-1}.

This region comprises the fingerprint region of the tropolonate ion and contains various ligand stretching and deformation modes. A number of these bands are characteristic for all tropolonate complexes and afford easy recognition of the complexes.

Two (or in some cases three) bands occur above 1200 cm^{-1}. They are assigned to C-H bending frequencies, but the possibility of C-C stretching frequencies occurring in this region cannot be excluded. A weak band occurs at 1075 cm^{-1}, bands of medium intensity at 975 cm^{-1} and 920 cm^{-1} and a strong band at 875 cm^{-1}. These bands are all characteristic of the metal tropolonate spectra and are probably out of plane C-H deformations, as assigned by Ikegami[17-19] for tropolone itself. Similarly, the two bands at 720 - 740 cm^{-1} and 750 - 770 cm^{-1} can also be assigned to ring deformation modes.

(iii) The Region 700 - 300 cm^{-1}.

This is the region in which the metal-ligand vibrations occur and most bands in this region show some degree of sensitivity to metal ion substitution. The significance of these metal sensitive bands has been

discussed in previous chapters dealing with transition metal tropolonates, non-transition metal tropolonates and lanthanide tropolonates.

Although these bands are labelled as νM-O bands they are not derived from pure M-O stretching (or bending) modes. This is unlikely as they all show varying degrees of sensitivity to both metal ion substitution and $[^{18}O]^-$ labelling. Tropolone itself has vibrational bands in this region, namely bands of weak intensity at 586 cm^{-1} and 537 cm^{-1} and bands of stronger intensity at 438 cm^{-1}, 380 cm^{-1} and 352 cm^{-1}. As these are regions where νM-O bands occur for the metal tropolonates, it seems reasonable to infer that there will be a coupling between the M-O stretching and bending vibrations and the ligand vibrations in this region.

The number of bands which occur in this region also varies according to the structure of the metal complexes. Thus an extra band occurs at 340 cm^{-1} for square planar complexes (CuT_2 and PdT_2) and in $Li[LnT_4]$ complexes, two extra bands occur at 360 cm^{-1} and 340 cm^{-1}, which do not occur in the $Na[LnT_4]$ complexes. For the LnT_3 complexes of La through to Ho there are six metal sensitive bands below 700 cm^{-1}, while for the complexes of Er through to Lu, which have a different structure from the first set, there are only five metal sensitive bands. The influence of the structure on the band pattern is more noticeable in this region, where the vibrations are all metal sensitive, than in the region above 700 cm^{-1} where all the vibrations are dependent on the ligand, which does not change structure from complex to complex.

6. FIRST TRANSITION SERIES METAL(II) COMPLEXES WITH NITROGEN DONORS.

The CF interpretation of the metal sensitive vibrations in a series of di- and trivalent metal tropolonates of the 3*d* elements has already been established. This interpretation can readily be extended to metal complexes of first transition series divalent metals and nitrogen donor ligands, where the vibrational spectra have been reported in many cases. A survey of these published results shows a similar trend of the metal sensitive vibrations to those of the metal tropolonates.

The predicted CFSE for the divalent metals is in the order Mn<Fe<Co<Ni>Cu>Zn and this order is followed by the metal sensitive vibrations, with the exception of Cu(II) which is nearly always found to be at higher frequency than that of Ni(II). This is caused by the Jahn-Teller distortion of the d^9 Cu(II) ion which produces tetragonal distortion or in some extreme cases square planar complexes. The $[CuCl_2py_2]$ complex is typical of the tetragonally distorted stereochemistry of Cu(II) complexes. The molecule has two Cu-N bonds of 2.02Å, two Cu-Cl bonds of 2.28Å and two Cu-Cl bonds of 3.05Å. The other members of this series are found to have regular polymeric octahedral structures. The changes in bond length are reflected in the vibrational spectrum where νCu-Cl occurs as a doublet at 237 cm^{-1} and 294 cm^{-1} (compared with νNi-Cl which occurs at 264 cm^{-1}).

Jahn-Teller distortion is apparent in the vibrational spectra of all the Cu(II) complexes with nitrogen donor ligands. In the case of the series $[Mpy_2(NCS)_2]$(M=Mn,Fe,Co,Ni,Cu,Zn) which have polymeric

octahedral structures, all the members, except Cu(II), have two bands which are assigned to νM-N and νM-(NCS). Cu(II) has three bands, the lowest being lower than the corresponding band for Ni(II) and the highest being higher than the corresponding band for Ni(II). In some cases the distortion is sufficiently great to render the Cu(II) complex square planar and no extra bands are observed, but the extra stability is shown in the νCu-N vibrational bands which are greater than the corresponding νNi-N. In the series $[M(NH_3)_6]Cl_2$, which are monomeric octahedral, the analogous Cu(II) complex cannot be formed. However the complex $[Cu(NH_3)_4]Cl_2$ is square planar and νCu-N (420 cm^{-1}) is greater than νNi-N (334 cm^{-1}).

The greater stability, as shown by the metal sensitive vibrations, inherent in Jahn-Teller distortion of Cu(II) is similar to that of Mn(III). A relatively small distortion of 0.03 Å in the case of $[Mn(AA)_3]$ leads to a splitting of the νMn-O and an increase in stability. Thus it seems reasonable to assume that because of this distortion the Cu(II) complex will always have higher metal sensitive bands than Ni(II) giving rise to the order Mn<Fe<Co<Ni<Cu>Zn.

This order is similar to that of Irving and Williams[16] for the stability constants of divalent metal complexes. The stability constants are indirectly measurements of free energy changes ($-\Delta G=2.303\ RT\ \log_{10}\beta$) and thus have a correlation with strengths of the metal-ligand bonds and hence to those fundamental properties of the metal ion and ligand which influence the type and strength of bond formed. In particular the CFSE will

influence the strength of the bond and this, together with the Jahn-Teller distortion of Cu(II) will govern the relative metal-ligand bond strengths and stability constants. As the vibrational stretching frequencies are also dependent on bond strength and thus the influence of CFSE it is not surprising that they follow the same order for the divalent metals. Table 26 shows some stability constants for divalent metal complexes with nitrogen donors and the stability order is seen to be similar to that observed for the metal sensitive frequencies.

TABLE 26. Stability constants for divalent transition metal complexes with nitrogen donor ligands.

Ligand		Co	Ni	Cu	Zn
Ammonia[99]	log β_4	5.55	7.95	12.67	9.46
	log β_6	5.05	8.73		
Pyridine[100]	log β_2	1.54	2.83	4.29	1.45
Alanine [101]	log β_2	8.48	10.66	15.37	9.54
Leucine[102]	log β_2	8.07	10.14	15.35	7.37

Complexes of Co(II) are frequently tetrahedral, and Zn(II) complexes with nitrogen donors are nearly always tetrahedral. In the case of Co(II), where tetrahedral structures occur, the metal sensitive frequencies of Co(II) are higher than those of Ni(II). The CFSE of tetrahedral Co(II) (in terms of the ligand parameter δ) is double the octahedral value. At the same time the value of δ is approximately halved in the tetrahedral environment, so that the net change in stability is small. However the

lower coordination number in tetrahedral complexes would raise νCo-N relative to an octahedral complex, since the bonding capacity of the ion is spread over four bonds instead of six.

In the series of complexes $[Mpy_2X_2]$(X=Cl,Br), the chloride complex of Co(II) is polymeric octahedral while the bromide complex is tetrahedral. The chloride complex has νCo-N<νNi-N (224 cm^{-1} compared with 239 cm^{-1}). The bromide complex has νCo-N>νNi-N (250 cm^{-1} compared with 237 cm^{-1}). The aniline complexes of Co(II) provide a similar example.

The Zn(II) complexes are usually tetrahedral. As the Zn(II) ion has zero CFSE, any extra stability the Zn(II) complex has, will be due to the tetrahedral structure. It is seen from Table 27 that where Zn(II) has tetrahedral structure, νZn-N is comparable to νNi-N, whereas in the case of octahedral Zn(II) the νZn-N is significantly lower than νNi-N. Thus, in the case of the complexes $[Mpy_2X_2]$ (X = Cl,Br) and $[Man_2X_2]$ (X = Cl,Br,I) where Zn is tetrahedral, νZn-N is of comparable order to νNi-N. In the case of the hexamine complexes, where Zn(II) is octahedrally coordinated, νZn-N is significantly lower than νNi-N. As there is no CF effect in the Zn(II) ion, which has d^{10} configuration, the coordination number effect is the only factor which can influence the stability. Thus the lower coordination number of the tetrahedral structure tends to increase the bond strengths of νZn-N (because the bonding capacity of the Zn(II) ion is distributed over fewer bonds than in 6 coordination), raising the metal sensitive vibrations. The tetrahedral structure of Co(II) and Zn(II)

can therefore lead to deviations from the expected order of Mn<Fe<Co<Ni<Cu>Zn.

There are other bands in the spectra of these complexes which also follow the order found for the metal sensitive vibrations. The fact that these bands have a similar trend and not an opposite trend is of interest. The concept of bond summation is not upheld in these cases, as a series of adjacent bonds are all strengthened simultaneously. In metal hydrazine complexes the νN-N frequencies follow the same trend as the νM-N frequencies. Similar effects are observed for νC-N in $[Mpy_2(NCS)_2]$, N-H deformations in ammines and hydrazines and C-C in-plane deformations of heterocyclic aromatic nitrogenous bases. There is therefore no bond summation about the nitrogen. The influence of the metal is the dominant feature and is transmitted further than the metal-ligand bonds, to the ligand atoms themselves, although the shifts in the ligand vibrations are usually smaller than those observed for νM-N. The bands assigned to NH_3 rock in the ammine complexes and NH_2 rock in the hydrazine and amino acid complexes have shifts much larger than those normally observed in ligand bands. These bands all occur in the region between 700 - 500 cm^{-1} and it is possible that these rocking modes are coupled to metal-ligand vibrations.

TABLE 27. Vibrational data for complexes of transition metal(II) ions with nitrogen donors (cm^{-1}).

Complex[a]	Vibration	Structure[b]	Mn	Fe	Co	Ni	Cu	Zn	Ref.
M-N vibration									
$[M(NH_3)_2Cl_2]$	ν(M-N)	p.o.		415	423	435	480	421t	103
$[M(NH_3)_2Br_2]$	ν(M-N)	p.o.		424	432	434	486	414t	103
$[M(NH_3)_6]Cl_2$	ν(M-N)	m.o.	307	321	327	334	420[c]	300	104
$[M(NH_3)_6]Br_2$	ν(M-N)	m.o.	299	315	318	327		294	104
$[M(NH_3)_6]I_2$	ν(M-N)	m.o.	295	306	312	322		282	104
$[Mhy_2Cl_2]$	ν(M-N)	p.o.	343	369	388	409	440	385	55
								345	
$[Mhy_3](NO_3)_2$	ν(M-N)	p.o.			393	417		359	105
$[Man_2Cl_2]$	ν(M-N)[d]	p.o.	386		415t	388	430	402t	106
$[Man_2Br_2]$	ν(M-N)[d]	p.o.	367		412t	386	424	400t	106
$[Man_2I_2]$	ν(M-N)[d]	p.o.	361		410t	361	424	396t	106
$[Mpy_2Cl_2]$	ν(M-N)[e,f]	p.o.	212	219[g]	224[g]	239[g]	268	220t	107
$[Mpy_2Br_2]$	ν(M-N)	p.o.	212		250t	237[g]	269	220t	107
$[Mpy_4Cl_2]$	ν(M-N)	m.o.			225	242			108
$[Mpy_2(NCS)_2]$	ν(M-N)[e]	p.o.	<200	200	213	229	256	227t.	109
							214		
	ν(M-NCS)[e]		254	261	268	280	319	312t	109
								268t	

TABLE 27 continued:

Complex[a]	Vibration	Structure[b]	Mn	Fe	Co	Ni	Cu	Zn	Ref.
M-N vibration									
$[Mpy_4(NCS)_2]$	ν(M-N)	m.o.	195	203	212	233	245		108,109
	ν(M-NCS)[e]		253	267	270	285	311		109
$[M(quin)_2Cl_2]$	ν(M-N)	p.o.	196		226t	223	259	205t	108
$[M(alanine)_2]$	ν(M-N)	p.o.			322	328	335	305	110
$[M(leucine)_2]$	ν(M-N)	p.o.			312	323	400s	314	111
							388s		
Representative M-Sensitive ligand vibrations									
$[M(NH_3)_2Cl_2]$	NH_3rock[h]	p.o.		624	645	676	716	685t	103
$[M(NH_3)_2Br_2]$	NH_3rock[h]	p.o.		617	639	670	720	680t	103
$[M(NH_3)_6]Cl_2$	NH_3deg.def.	m.o.	1592	1597	1602	1607		1596	104
	NH_3sym.def.		1134	1151	1163	1175		1145	104
	NH_3rock		617	641	654	680	709[c]	645	104
$[M(NH_3)_6]Br_2$	NH_3deg.def.	m.o.	1589	1595	1600	1603		1592	104
	NH_3sym.def.		1145	1159	1174	1188		1156	104
	NH_3rock		606	625	647	672		636	104

TABLE 27 continued:

Complex[a]	Vibration	Structure[b]	Mn	Fe	Co	Ni	Cu	Zn	Ref.
Representative M-Sensitive ligand vibrations									
$[M(NH_3)_6]I_2$	NH_3deg.def.	m.o.	1582	1592	1595	1597		1594	104
	NH_3sym.def.		1155	1182	1189	1205		1179	104
	NH_3rock		592	617	626	654		621	104
$[Mhy_2Cl_2]$	ν(N-N)	p.o.	960	964	974	978	985	976	55
	NH_2as.rock		590	607	625	649	682	625	55
	NH_2sym.rock		518	553	582	613	658	580	55
$[Mhy_3](NO_3)_2$	ν(N-N)	p.o.			964	973		972	105
$[Man_2Cl_2]$	ν(M-Cl)	p.o.	227		318t	238	306	294t	106
					299t				
$[Mpy_2Cl_2]$	ligand[i.j]	p.o.	627	629	631	634	644	639t	107
	ligand[k.l]		419	424	429	439	441	422t	107
	ν(M-Cl)		231		234	264	294	331t	108
							237	298t	
$[Mpy_2Br_2]$	ligand[i]	p.o.	628		642t	634	644	639t	107
	ligand[k]		422		422t	442	441	422t	107
					416t				

TABLE 27 continued:

Complex[a]	Vibration	Structure[b]	Mn	Fe	Co	Ni	Cu	Zn	Ref.
Representative M-sensitive ligand vibration									
$[Mpy_4Cl_2]$	ligand[i]	m.o.			623	627			108
$[M(\gamma\text{-pic})_2Cl_2]$	ligand[i]	p.o.	535		554t	546	550	555t	112
								550t	
$[M(\gamma\text{-pic})_4Cl_2]$	ligand[i]	m.o.	533		538	541			112
$[M(\gamma\text{-pic})_4Br_2]$	ligand[i]	m.o.	542	536	539	541			112
			535						
$[Mpy_2(NCS)_2]$	ligand[i.e]	p.o.	627	629	628	630	640		109
	ν(C-N)[m]			2062	2088		2096	2075t	113
$[Mpy_4(NCS)_2]$	ligand[i.e]	m.o.	625	623	625	627	636		109
	ν(C-N)		2066	2068	2072	2079	2080		109
$[M(quin)_2Cl_2]$	ligand[i]	p.o.	621		635t	631	637	635t	108
						621		623t	
	ν(M-Cl)		246		312t	263	332	316t	108
								300t	
$[M(alanine)_2]$	NH_2rock	p.o.			565	641	665	635	110
$[M(leucine)_2]$	NH_2rock	p.o.			579	625	655s	645	111

TABLE 27 continued ...

[a]Ligand abbreviations: hy=hydrazine; an=.aniline; py=pyridine; quin=quinoline; γ-pic= γ-picoline.

[b]p.o.=polymeric octahedral; m.o.=monomeric octahedral. Exceptions (other than tetragonal Cu(II) are indicated by suffixes: t=tetrahedral; s=square planar.

[c]$[Cu(NH_3)_4]Cl_2$, frequency from ref. 114.

[d]Assignments of M-N frequencies in aniline complexes are by no means certain. A lower frequency band also quoted as ν(M-N) exhibits a roughly inverse relationship to that quoted here.

[e]Frequencies are in good agreement with those in ref. 108.

[f]Frequency for Cr(II) complex = 219 cm^{-1}.

[g]Our assignment on the basis of ref. 108.

[h]A lower frequency NH_3 rocking frequency exhibits the same trends.

[i]C-C in-plane bend of heterocyclic ring[108]

[j]Frequency for Cr(II) complex = 640 cm^{-1}.

[k]C-C out-of-plane bend of heretocyclic ring[108]

[l]Frequency for Cr(II) complex = 440 cm^{-1}.

[m]Frequencies are not in good agreement with those in ref. 109 but appear to have been determined with greater precision.

7. THE VIBRATIONAL SPECTRA OF METAL COMPLEXES OF ETHYLENEDIAMINE AND N-SUBSTITUTED ETHYLENEDIAMINES.

(i) The Tris(ethylenediamine) Metal Sulphates.

The problem of assigning metal sensitive bands to the vibrational spectra of ethylenediamine complexes has already been examined by several workers[25-35]. Most of these workers have attempted to assign a particular band in the spectra to the metal-nitrogen vibration of the molecule. However there might be several vibrational bands in the spectra which show some degree of metal sensitivity. An attempt is made here to investigate the bands showing metal sensitivity by employing CF effects. In order to use these CF effects, a reasonably large series of related isostructural compounds should be studied so that any trend in the spectra might be clearly distinguished and so that no structural changes might influence the observed trends.

Such a series is the tris ethylenediamine complexes of divalent metal sulphates, which are particularly interesting in that the copper complex can be synthesized[115]. Normally it is not possible to prepare tris complexes of copper because of the strong Jahn-Teller distorting forces which usually counter the binding of a third ligand. Tris complexes have an added advantage in the case of ethylenediamines in that the anion lies outside the coordination sphere and there is, therefore, unlikely to be any interaction between the anion and the metal ion, which might influence any observable trends.

The vibrational spectra of the series of complexes $[M(en)_3]SO_4$ (M=Mn, Co, Ni, Cu, Zn) have been recorded and

show five bands below 700cm^{-1} which shift in the order similar to that of the CFSE and which could therefore be assigned to metal sensitive vibrations of the molecule (Fig. 21). The band previously assigned[25-33] to the metal-nitrogen vibration, in the 500-550 cm^{-1} region shows the expected shift indicating that it is sensitive to metal substitution. However this band is no more metal sensitive than any of the other bands which show some metal sensitivity, and is certainly less metal sensitive than the bands at 300 cm^{-1} and at 680 cm^{-1}. The vibrational spectrum of ethylenediamine dihydrochloride shows bands at 330 and 476 cm^{-1} which could imply that the vibrations at 300-350 cm^{-1}, 490-520 cm^{-1} and 500-550 cm^{-1} are due to ligand vibrations coupled to some metal-ligand vibration. The vibration[34,35] in the 390-410 cm^{-1} region occurs where no ligand vibration is present and this is the band which is assumed in more recent publications to be the metal-nitrogen vibration. However, the metal sensitivity of this band is no greater than any of the other bands below 700 cm^{-1}.

The band in the 670-730 cm^{-1} region has been assigned by most previous workers to the NH_2 rocking mode (δNH_2). This band shows more sensitivity to change of metal ion than most of the other bands below 700 cm^{-1}. Metal complexes with amine ligands (ammonia, aniline etc.) all seem to show a similar effect to that observed here for the ethylenediamine complexes, namely that the shift on changing metal ion is much greater for the band assigned to an NH_2 rock than for the bands assigned to metal-nitrogen vibrations (see Table 27). Thus it seems likely that this band is also coupled to some metal-ligand vibration and also that the influence of the

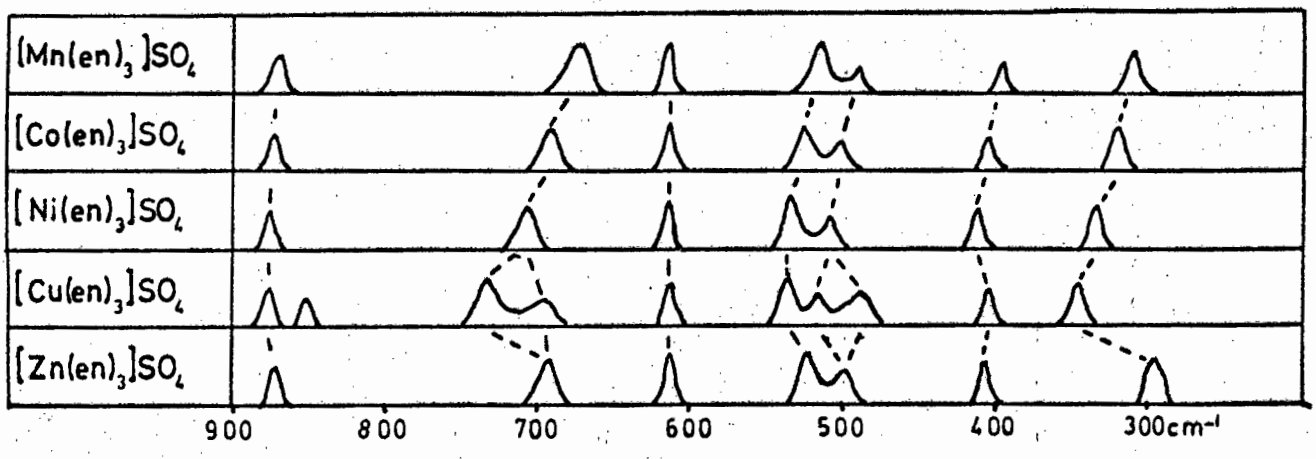


Fig.21. Vibrational spectra (900-300cm^{-1}) of tris(ethylenediamino)metal(II) sulphates.

metal ion on the metal-ligand bonds might extend further to influence the N-H bonds. This is not unusual as a similar effect is observed for the metal hydrazine complexes[55] where changing the metal ion has some influence on most of the ligand vibrations. However no other band in the spectra associated with an NH_2 vibrational mode shows any metal sensitivity so that it is difficult to decide how much influence the metal ion does have on the N-H bond strength or whether the observed metal sensitivity is entirely due to coupling with a metal-ligand vibration.

Of particular interest is the vibrational spectrum of the copper complex. As has already been stated, octahedral coordination to a copper ion is unusual because of the strong tetrogonal distorting forces. However, when the copper ion is actually in an octahedral environment, the ligands tend to oppose the distorting force so that the associated stabilization energy of the distortion is reduced (compared to bis complexes for example). This is particularly noticeable in compounds such as the bipy and phen adducts of CuT_2 or in $[Cu(bipy)_3]^{2+}$ and $[Cu(phen)_3]^{2+}$ complexes[60] where the ligands are rigid. The ethylenediamine ligand is fairly flexible and thus should be able to accommodate distortion fairly readily. It would thus be expected that the $[Cu(en)_3]^{2+}$ ion would show quite a large distortion compared to the abovementioned octahedral copper complexes.

The vibrational spectrum of $[Cu(en)_3]SO_4$ shows splitting of two sets of bands, namely the band in the 670-730 cm^{-1} region and the two bands in the 490-550 cm^{-1} region, compared to the spectra of the other tris ethylenediamine complexes. This splitting of the vibrational

bands is indicative of a decrease in the symmetry of the molecule caused by a distortion of the bonds (as is observed for MnT_3). Using the mean of the split bands in those cases where splitting occurs, it is seen that the two most metal sensitive bands, namely at 300-350 cm^{-1} and 670-730 cm^{-1} have the order Mn<Co<Ni<Cu>Zn, while the other three bands have the order Mn<Co<Ni>Cu>Zn. This suggests that there might be a difference in the coupling involved in the various vibrations and this might have differing influences on the various bands.

A crystal structure of the $[Cu(en)_3]SO_4$ molecule[116] reveals that there is very little difference in the bond lengths of the Cu-N bonds which does not suggest any significant distortion. It is pointed out that as the molecule is found, crystallographically, to have large thermal parameters, there might be some justification for assuming the existence of a dynamic Jahn-Teller effect. Nevertheless this finding from the crystal structure is surprising as the distortion would have been expected to be larger than that observed, especially in view of the splitting found in the vibrational spectrum.

(ii) Substituent Effects with N-substituted Ethylenediamines.

The bis and mono ethylenediamine and N-substituted ethylenediamine complexes of Cu(II) ions ($[Cu(ligand)_2]X_2$ and $[Cu(ligand)X_2]$) were studied in order to determine the influence of the substituent on the metal sensitive bands in the vibrational spectra.

As was observed for the tris ethylenediamine metal sulphate complexes, the vibrational spectra of the complexes

with substituted ethylenediamines have several bands in the region below 700 cm^{-1}, most of which could have some metal sensitivity. The situation is more complicated for the substituted ethylenediamine complexes as the band pattern alters with change of substituents. The ligands themselves have varying band patterns in this region, caused by changes of symmetry and structure which result in different vibrations occurring (particularly skeletal vibrations). These ligand bands could couple with the metal-ligand vibrations giving rise to the varying band patterns in the spectra of the differently substituted complexes.

For example, ethylenediamine dihydrochloride, as has been mentioned, has vibrational bands at 330 and 476 cm^{-1} which couple with metal-ligand vibrations in the complexes and show metal sensitivity. *Sym*-N,N´-dimethylethylenediamine dihydrochloride has two bands at 471 and 480 cm^{-1} and 1,3-diaminopropane dihydrochloride has bands at 428 and 450 cm^{-1} and when these ligand bands couple they will produce different band patterns.

The variation in band pattern of the variously substituted ethylenediamine complexes gives rise to difficulties in assigning trends caused by substituents. This problem can be overcome to some extent by studying the band in the 350-400 cm^{-1} region which has previously been assigned to the metal-nitrogen vibration[34,35]. As no ligand vibrations occur in this region of the spectra, it has been assumed that this band is free from coupling effects and thus will be neither split nor shifted by coupling with any ligand vibrations. It is however unfortunate that this band is not amongst those which showed the greatest metal sensitivity in the spectra

of the tris ethylenediamine metal sulphate complexes.

Both $[Cu(ligand)_2]X_2$ and $[Cu(ligand)X_2]$ complexes were chosen for this study as a reasonable number of analytically pure complexes could be synthesized and because the 350-400 cm^{-1} band (which is used to observe substituent effects) has been previously assigned[34,35]. Both the halogen anions used in the various complexes (chloride and bromide) are involved to some extent, in coordination with the Cu(II) ion. In the case of the $[Cu(ligand)_2\ X_2]$, the interaction is in the axial positions so that the molecule has an octahedral structure. In the case of the $[Cu(ligand)X_2]$, the halogen ions are in the trans positions to the ligand so that the metal-ligand bonds assume planarity (although the ligand is gauche and therefore is not in this plane). Further interaction takes place with the other molecules, in the axial positions, so that the Cu(II) ion could be six coordinate.

The anions have an influence on the metal sensitive vibrations of the complexes, depending on the extent of their interaction with the Cu(II) ion. In general, the chloride containing complexes are found to have metal sensitive bands of higher frequency than those of bromide containing complexes. A change of halogen anion does not however change the band pattern of the vibrational spectra, only the position of the bands. The influence of the anion on the vibrational spectra of the copper complexes has been previously examined[34,35]. For the $[Cu(ligand)X_2]$ a trans effect has been found to be operative so that the Cu-N bond is strengthened on change of anion. However little mention has been made of any substituent effect of the ligand on the vibrational spectra of these complexes.

The alkyl substituents on the nitrogen atoms of the ethylenediamine are expected to increase the electron density of the nitrogen due to their greater inductive electron releasing properties (relative to hydrogen). This electron releasing capacity increases with increasing chain length of the alkyl substituent. This electron releasing capacity is shown in the σ values (Taft[117,118]) obtained for alkyl substituents in aliphatic compounds, where the values are given as H = +0.49, Me = 0, Et =-0.10 and nPr = -0.115 (positive values signify electron withdrawal and negative values, electron release).

These electron releasing properties should lead to a greater basicity of the ligand and in turn to stronger binding between the ligand and metal ions. There is however another consideration, namely that of the steric hindrance encountered as the alkyl chain length increases, which could offset the increased basicity. It has been demonstrated[46,119] that although alkyl substituents on one nitrogen of ethylenediamine increases the base strength, the first, second and total formation constants of the substituted ethylenediamines with Ni(II) and Cu(II) are all smaller than the corresponding constants for ethylenediamine. Thus it appears that the steric crowding imposed by the substituents during complex formation are of greater importance than the increased electron donating ability of the ligand atoms.

A similar effect has been noted in spectroscopic determinations of Dq for complexes of the type $[Ni(ligand)_3](ClO_4)_2$[120]. The value of Dq decreases with increasing alkyl substitution, instead of increasing as would be expected on the basis of greater electron donating

capacity of the ligand. It is likely that steric effects hinder close approach of the ligands to the metal ion, particularly for these complexes where three comparatively bulky ligands all approach the metal ion.

The order of increase of the 350-400 cm^{-1} band in the vibrational spectra of the various substituted complexes is

DAP<NN'Meen<NNMeen<en<NMeen<NEten<NPren

for the $[Cu(ligand)_2]X_2$ complexes and

DAP<NN'Meen<NMeen<en<NNMeen<NEten<NPren

for the $[Cu(ligand)X_2]$ complexes (see Fig. 22). The order for both sets of complexes is similar except for NNMeen and NMeen. If the ligands which are substituted by only one alkyl group on one of the nitrogens, are considered, then the order can be seen to be that predicted on the basis of electronic considerations only, namely

NMeen<NEten<NPren.

This order corresponds to that calculated for the σ values for these substituents[117,118], which are based solely on electronic properties. However it is contrary to the previous observations from determination of formation constants[46,119] and spectroscopic values of Dq[120], where steric hindrance appeared to have a dominating role.

It is possible that steric hindrance has reduced importance in determining bond strength in the solid state, compared to its influence in solution studies. This could account for the reversal of the order from that observed for the formation constant studies, to that observed here for the vibrational spectra of the solid complexes. Certainly in the case of the $[Cu(ligand)X_2]$ complexes, the steric

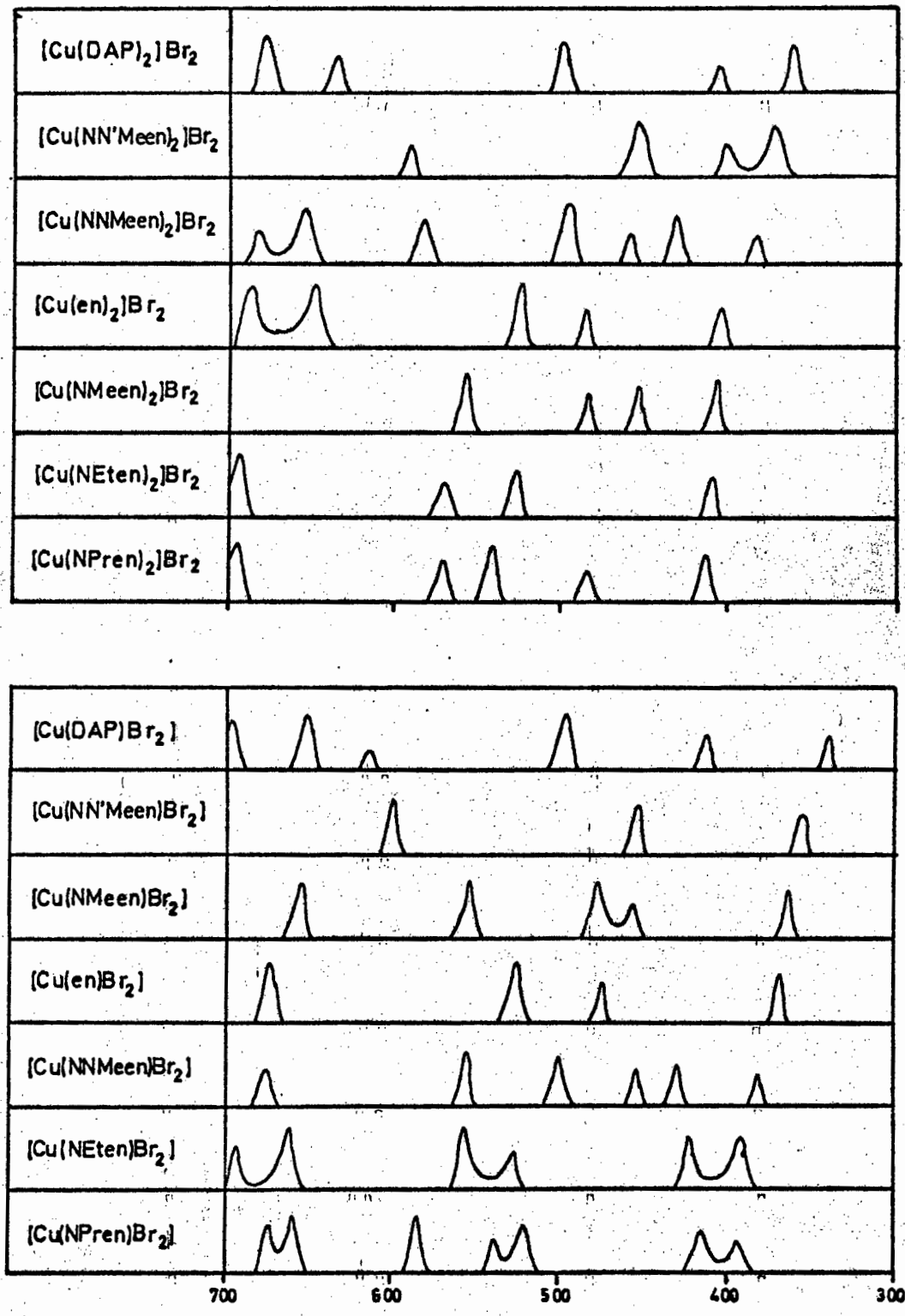


Fig. 22. Vibrational spectra (700-300cm^{-1}) of the N-substituted ethylenediamines.

hindrance could be comparatively small and the Cu(II) is unlikely to suffer from crowding by the ligand.

This could explain the change in order of the NNMeen ligand in proceeding from the [Cu(ligand)X_2] complex to the [Cu(ligand)$_2$]X_2 complex. In the former complex, with only one ligand, the bulky tertiary amine group should not experience great steric hindrance in its approach to the metal ion. Thus the electron releasing effect of the two methyl groups might dominate, causing a stabilization of the metal-ligand bonds. In the second complex, with two ligands, the steric hindrance will be greater resulting in a weakening of the metal-ligand bonds.

Of all the complexes, those containing DAP have the lowest frequency metal sensitive bands. DAP differs from the other ligands, in that it chelates with metal ions to produce 6-membered chelate rings as opposed to the 5-membered rings of the ethylenediamines. It has been well established that 6-membered rings are generally less stable than 5-membered rings and this has been confirmed by determinations of the formation constants for DAP complexes and ethylenediamine complexes[121].

In conclusion, it can be seen that an investigation of substituent effects for ethylenediamine complexes by vibrational spectroscopy has several difficulties. There is some difficulty in choosing a band to study due to changing band patterns with changing substituent. Further, the influence of the substituents is dependent upon two opposing effects, namely the increasing electron releasing ability of the substituent and the increasing bulk of the substituent leading to steric hindrance. This has led to

a difference in the substituent effects observed here using vibrational spectra, and those effects determined by other techniques.

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